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AIR POLLUTION: CONTROL TECHNIQUES FOR NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

NATO Committee on the Challenges of Modern Society

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Environmental Protection Agency
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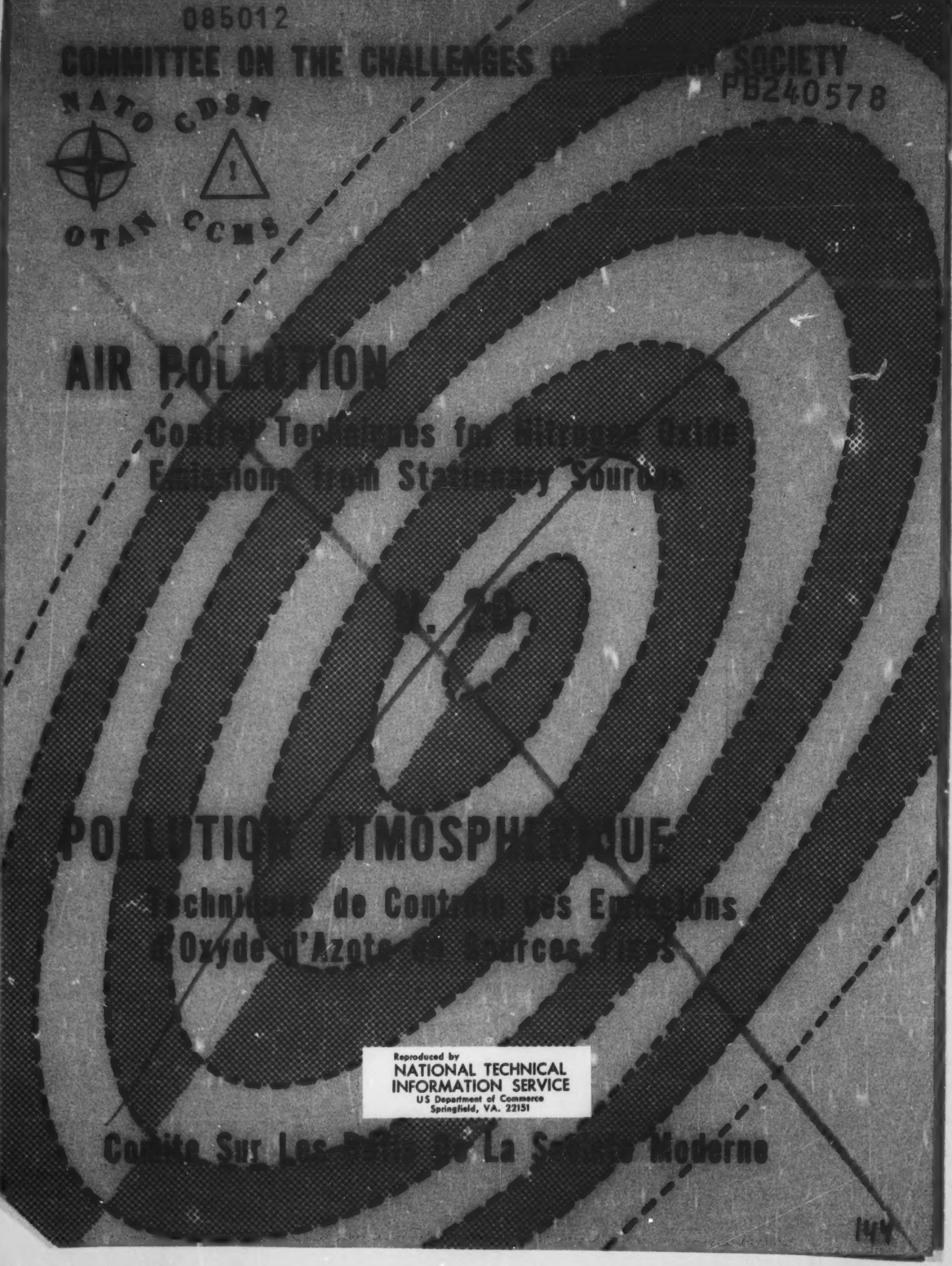

AIR POLLUTION

Control Techniques for Nitrogen Oxide Emissions from Stationary Sources

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POLLUTION ATMOSPHERIQUE

Techniques de Contrôle des Emissions d'Oxyde d'Azote des Sources Fixes

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FOR
NITROGEN OXIDE EMISSIONS
FROM STATIONARY SOURCES

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PREPARED FOR
THE COMMITTEE ON THE CHALLENGES
OF MODERN SOCIETY

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October, 1973

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FOREWORD

This document is a compilation of information on methods for the control of nitrogen oxide emissions that was assembled by the Expert Panel for Air Pollution Control Technology, The Committee on the Challenges of Modern Society, NATO, for distribution to the member countries.

The Chairman of the Expert Panel wishes to acknowledge the efforts of scientists from the pilot countries, scientists from observer countries, and the many other persons who assisted in the preparation of this document and the four companion volumes: Control Techniques for Particulate Air Pollutants, Control Techniques for Carbon Monoxide Emissions from Stationary Sources, Control Techniques for Sulfur Oxide Air Pollutants, and Control Techniques for Hydrocarbon and Organic Solvent Emissions from Stationary Sources.

Thanks are due the Environmental Protection Agency of the United States for permission to use their document, Control Techniques for Nitrogen Oxide Emissions from Stationary Sources, which was published in 1970, as a basis for this effort. Representatives from this agency deserve special recognition.

Major contributions were made by a team of scientists from the Federal Republic of Germany under the direction of Dr. Dieter Hartmann. These contributions were invaluable to the success of the effort.

Recognition should also be given to the team from the Research Triangle Institute, Research Triangle Park, North Carolina, USA, for their efforts in literature searches, writing, and editorial work.

Lastly, acknowledgment should be given to those secretaries and other support personnel who have made the panel effort possible.

John K. Burchard, Ph.D.
Panel Chairman

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SUMMARY

Nitrogen oxides (NO_x) refer to two gaseous oxides of nitrogen, nitric oxide (NO) and nitrogen dioxide (NO_2). These pollutants originate with the combustion of fossil fuels or with the manufacture and use of nitric acid.

During the combustion of fossil fuels, nitrogen and oxygen combine in accordance with the following equation:

$$N_2 + O_2 \rightleftarrows 2\ NO$$

Nitric oxide reacts with oxygen as follows:

$$NO + 1/2\ O_2 \rightleftarrows NO_2$$

SOURCES OF NITROGEN OXIDES

Mobile sources, the largest single source category, contribute over 40 percent of all the man-made NO_x emitted in the United States. The second largest source is electric power generation, which is responsible for nearly 20 percent of all man-made NO_x. About 40 percent of the NO_x emitted from stationary installations is attributed to electric power generating plants.

About 1 percent of the total man-made NO_x emitted to the ambient air of the United States is formed by chemical processes, mainly related to the manufacture and use of nitric acid.

Table 1 summarizes the estimated emissions of NO_x by source for 1970.

Table 1. SUMMARY OF U.S. NITROGEN OXIDES EMISSIONS, 1970

Source	Gkg/yr	Percent of total
Transportation	10.6	51.3
a. Motor Vehicles	8.3	39.9
1. Gasoline	7.1	34.2
2. Diesel	1.2	5.7
b. Aircraft	0.36	1.8
c. Railroads	0.09	0.4
d. Vessels	0.18	0.9
e. Non-highway use of motor fuels	1.7	8.3
Fuel Combustion in Stationary Sources	9.1	43.8
a. Coal	3.5	17.1
b. Fuel Oil	1.2	5.7
c. Natural Gas	4.1	19.7
d. LPG & Kerosene	0.18	0.9
e. Wood	0.09	0.4
Industrial Processes	0.18	0.9
Solid Waste Disposal	0.36	1.8
Miscellaneous	0.45	2.2
a. Forest Fires	0.18	0.9
b. Structural Fires	N	N
c. Coal Refuse	N	N
d. Agricultural	0.27	1.3
Total	20.69	100.0

CONTROL TECHNIQUES

Methods of controlling NO_x emissions can be divided into two broad categories--those which reduce or prevent the formation of NO_x and those which extract NO_x from the off-gases. The first category is mainly applicable to the combustion of fossil fuels and usually involves a modification of the combustion process. Control methods in the second category are applicable to both combustion and chemical processes but have been more successful for chemical process off-gases.

Combustion Process Modification

In fossil fuel combustion, NO_x emissions may be reduced by switching to a fuel with a lower nitrogen content. The use of nuclear energy for electric power production is expected to grow rapidly in future years. Nitrogen oxides are not emitted since the combustion of fossil fuels is not involved.

NO_x formation in a furnace or boiler increases as the heat release rate increases. Emissions are reduced if a low heat release rate can be maintained.

Low-excess-air operation has reduced NO_x emissions from oil- and gas-fired power plant boilers by 30 to 60 percent, depending upon the percentage of excess air, the design of the boiler, and the type of firing.

Laboratory results of the flue-gas recirculation technique show sizable reductions in NO_x emissions, particularly when used in combination with low-excess-air firing; however, tests on boiler emissions are inconclusive. Recirculated gases are injected directly into the flame zone.

Control of NO_x by steam and water injection is based on lowering the peak flame temperature and diluting the combustion gases. This method requires further development and may involve loss in efficiency, but it has been found to reduce NO_x emissions from internal combustion engines.

Two-stage combustion in oil- and gas-fired boilers has reduced NO_x emissions from power plant boilers by 30 to 50 percent. A modified two-stage combustion technique combined with low-excess-air firing has reduced the stack-gas NO_x concentration emitted by two 750-megawatt gas-fired power plant boilers from 1500 to 175 parts per million (ppm).

New burner types which reduce NO_x formation are in various stages of development.

Fluidized-bed combustion has been successful in reducing NO_x emissions in laboratory experiments but has not been commercially proven.

Oxygen enrichment shows promise of reducing NO_x formation during combustion but the method requires further investigation of economic aspects.

Industrial, commercial, and household heating requirements contribute to above-average NO_x concentrations in urban areas. These requirements may in part be shifted to central electric-power stations with NO_x emission controls.

Recent developments in NO_x control from combustion processes include the use of an electric field in the flame zone, the use of fuel-oil additives, and "total incineration" processes which operate at temperatures sufficiently low to prevent NO_x formation.

Gas Cleaning

Methods which have had varying degrees of success in extracting NO_x from flue gases include limestone wet scrubbing, Reinluft char process, and modified lead chamber process. Other techniques under investigation include selective reduction of NO_x by ammonia and catalytic oxidation with various catalysts.

Techniques which have been used for chemical process off-gases include lime/limestone scrubbing, caustic scrubbing, and catalytic reduction and abatement. Developmental techniques for chemical off-gas cleaning include molecular sieves, absorption in acid, sorption by ion exchange resins, and NO_x incineration.

EMISSION FACTORS

Emission factors may be used to estimate emissions from sources for which accurate stack test results are unavailable. Process emission factors for some selected source types are presented in Chapter 5.

Data which apply to the Federal German Republic are referenced as "BRD" (Bundes Republik Deutschland).

1. INTRODUCTION

Nitrogen oxides in the atmosphere are known to have many adverse effects upon health and welfare, and reduction of emissions of these pollutants is of prime importance to any effective air pollution abatement program. This document has been prepared to summarize current information on nitrogen oxide air pollutants--sources and methods of control.

Nitrogen oxides originate from a variety of sources, and the emissions vary widely in physical and chemical characteristics. The many agricultural, commercial, domestic, industrial, and municipal sources o these air pollutants are described individually in this document. The nature and quantities of the emissions from the various processes are discussed, and methods of control that have been successfully applied are listed.

The control techniques described herein represent a broad spectrum of information from many engineering and other technical fields. The devices, methods, and principles have been developed and used over many years, and much experience has been gained in their application. They are the techniques generally applicable to the broad range of nitrogen oxide emission control problems.

A tabulation of emission factors from which overall emissions for the various sources can be estimated is presented. Although the factor are normally for sources with no control, where applicable, emission factors are given for representative types of control.

2. BACKGROUND INFORMATION

2.1 DEFINITIONS

Nitrogen oxides in the atmosphere are known to be involved in the formation of photochemical smog of the Los Angeles type through complex reactions with hydrocarbons and other pollutant gases under the influence of sunlight.

Two oxides of nitrogen are important in the atmosphere: nitric oxide (NO) and nitrogen dioxide (NO_2). Five more oxides of nitrogen are known: NO_3, N_2O, N_2O_3, N_2O_4, and N_2O_5. The oxides NO_3 and N_2O_4 are too unstable to exist at atmospheric conditions; N_2O_3 and N_2O_5 are the anhydrides of nitrous and nitric acid, respectively; and N_2O, the anesthetic known as "laughing gas," is a stable compound and can support combustion.

The term NO_x is used generally to represent the gaseous pollutants NO_2 and NO, expressed as NO_2. It is known that NO is oxidized to NO_2 by oxidants, including oxygen in the air. Special precautions in sampling and analysis are required, therefore, to get reliable measurements of NO. This difficulty is serious enough to cast doubt on most of the data in the older literature since the ratio of NO to NO_2 may not be reliable.

Nitrous oxide (N_2O) is formed largely from the decomposition of nitrogen compounds by soil bacteria. It has a mean concentration of about 0.25 ppm in the atmosphere.[1] Nitric oxide and nitrogen dioxide are formed under high-temperature conditions such as the burning of fossil fuels, and in much larger amounts by various biological reactions in nature but in low concentrations. Most of the NO_x formed by man is nitric oxide, which is oxidized to the more toxic and irritant nitrogen dioxide by the oxygen of the air, or, much more easily, by photochemically reactive hydrocarbons in the presence of sunlight.

2.2 MAJOR SOURCES

Oxides of nitrogen (NO_x) are emitted from both stationary and mobile sources in roughly equal proportions on a nationwide basis. They are emitted in significant amounts as the result of the fixation of nitrogen in combustion processes but not directly in proportion to the nitrogen content of fossil fuels burned.

Stationary sources of oxides of nitrogen are primarily fossil-fuel combustion sources and, to a lesser extent, other industrial stationary sources. Fuel type, equipment operation and design, and other variables influence the levels of NO_x emitted by individual sources to the extent that currently available emission factors have only a broad and generalized applicability. A number of potential techniques being developed for controlling these emissions are based either on principles that prevent the formation of NO_x or on methods for the removal of NO_x from stack or tail gases. Except for a few chemical reactions that occur when the only reactive constituent of the tail gas is NO_x, the feasible methods appear to be confined to those that control nitrogen oxides and sulfur oxides emissions simultaneously.

Noncombustion processes contribute only a small proportion of total NO_x emissions but can present a serious local hazard. Control technology in this area has been the subject of intensive research, particularly in the manufacture and uses of nitric acid wherein NO_2 is a process raw material. Control technology via combustion modification

Table 2-1. NITROGEN OXIDE EMISSIONS BY SOURCE CATEGORY, 1970[2]

	Quantity (Gkg)	Percent of total
Transportation	10.6	51.0
Fuel combustion stationary)	9.1	44.0
Industrial processes	0.18	1.0
Refuse disposal	0.36	2.0
Miscellaneous	0.45	2.0
	20.69	100.0

in oil- and gas-fired processes has been applied, and this method is recommended for further application and development. Several other potential techniques must await the results of further research and development in controlling nitrogen oxide emissions from stationary sources.

An estimated 20.69 Gkg of nitrogen oxides were emitted from industrial, commercial, and domestic sources in the United States during 1970.[2] Table 2-1 shows the contribution to this total from each source category. Stationary fuel combustion and transportation are the largest emitters of nitrogen oxides.

REFERENCES

1. Goddy, R. M. and C.D. Walshaw. The Origin of Atmospheric Nitrous Oxide. Quart. J. Roy. Meteorol. Soc. 79 (342): 496-500, October 1953.

2. OAP Data File of Nationwide Emissions, 1970. National Air Data Center, Applied Technology Division, July 1972.

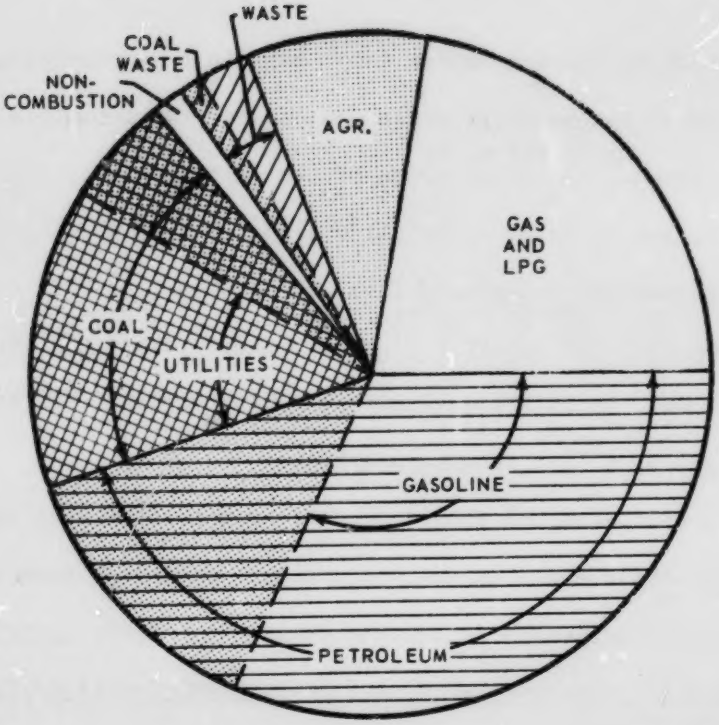
3. STATIONARY SOURCES OF NITROGEN OXIDES

Air pollution by nitrogen oxide (NO_x) emissions becomes progressively worse as population becomes more dense and demands for industrial combustion energy increase.[1] In urban areas of the United States, the concentration of NO_x averages 40 to 50 parts per billion (ppb),[2] which is much greater than the natural background level of 1 ppb; it is this difference that creates the need for control. The Air Quality Standards for NO_x (calculated as NO_2)[3] in the BRD are 600 $\mu g/m^3$ for threshold limit air pollution and 100 $\mu g/m^3$ for long-term exposure.

Figure 3-1 and Table 3-1 show the total amount of manmade NO_x generated in 1968 by both mobile and stationary sources. (Emissions from mobile sources are treated at length in another document: AP-66, Control Techniques for Carbon Monoxide, Nitrogen Oxide, and Hydrocarbon Emissions from Mobile Sources.) Stationary sources not involving combustion--mainly the manufacture and use of nitric acid--often produce highly concentrated, visible red-brown emissions, but these are only about 1 percent of total NO_x.

The largest sources are electric power plants and industrial combustion. Figure 3-2 presents a 1968 estimate of NO_x emissions from stationary installations in the United States. Coal, oil, and gas in power plants or boilers are compared in Table 3-2, and average emission factors on an equivalent (heating value) basis are given. These values vary widely in individual units (Section 5). Coal, with its large emission factors, accounts for approximately 39 percent of all NO_x from stationary installations in the United States, or 18 percent of the total shown in Table 3-1. The second largest source of NO_x emissions is natural-gas-driven compressors for oil and gas pipelines and gas plants--largely a nonurban source (Section 5).

Total estimated oxides of nitrogen emissions (NO_2) from mobile and stationary sources in the BRD, 1970, are shown in Fig. 3-3.



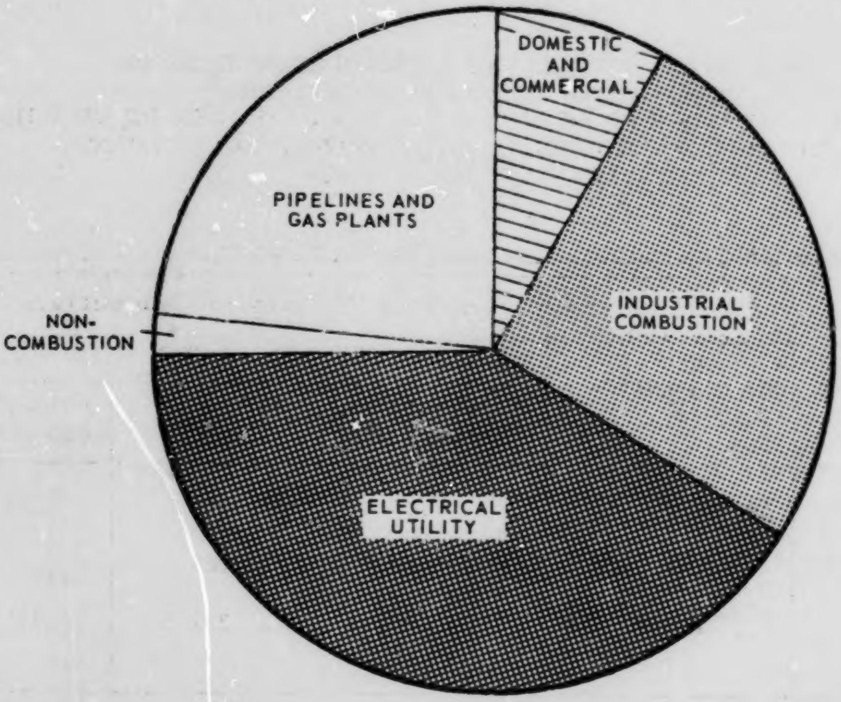
Fuel Type	NO$_x$ (Mkg)	
Gas and LPG	4 220	
Petroleum	8 500	
Auto/Gasoline		6 000
Coal	3 640	
Coal utilities		2 700
Waste burning	680	
Coal wastes		170
Industrial non-combustion	180	
Agricultural, wood, and forest Fires	1 680	
U. S. Total	18 800	

Figure 3-1. Total estimated oxides of nitrogen emissions from mobile and stationary sources by fuel type in United States, 1968.

Table 3-1. ESTIMATES OF NITROGEN OXIDE EMISSIONS IN THE UNITED STATES, BY SOURCE, 1968[3]

(Mkg/yr)

Source	Estimated emissions
Mobile fuel combustion	
Motor vehicles:	
Gasoline	6 000
Diesel	546
Aircraft	36
Railroad	364
Vessels	273
Non-highway users	273
Stationary fuel combustion	
Coal	3 640
Fuel oil	1 010
Natural gas	4 220
Wood	209
Solid waste	
Open burning	410
Conical incinerators	16
Municipal incinerators	17
On-site incinerators	63
Coal waste banks	173
Forest burning	1 092
Agricultural burning	255
Structural fires	21
Industrial processed	182
Total	18 800



Type of installation	NO_x (Mkg)
Electrical utility	3 640
Industrial combustion	2 660
Pipelines and gas plants	2 080
Domestic and commercial	750
Non-combustion	180
U. S. Total	9 310

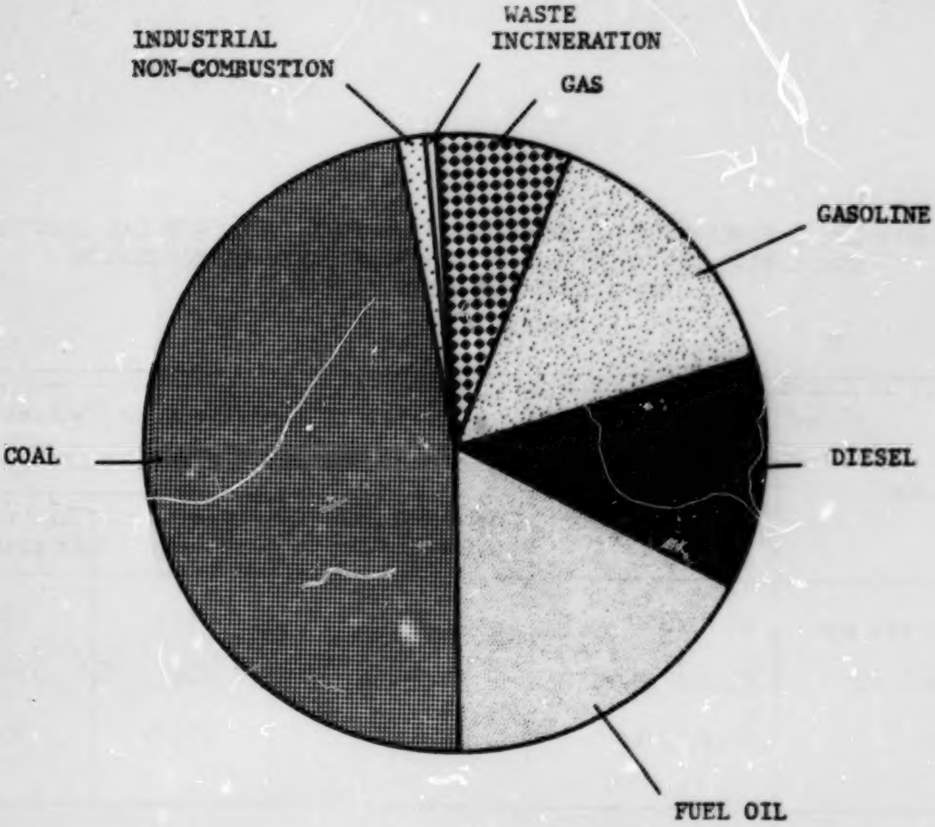
Figure 3-2. Total estimated oxides of nitrogen emissions from stationary installations by type of use in United States, 1968.

Table 3-2. COMPARISON OF EMISSIONS FROM COAL, OIL, AND GAS USED IN STATIONARY INSTALLATIONS IN UNITED STATES, ON EQUIVALENT HEATING VALUE BASIS, 1968[2]

(pkg/J)

Fuel	Equivalent heating value[7]	Average NO_x emissions in boilers and power plants		
		Household and commercial[a]	Industry	Electric generation
Natural gas	39 MJ/m^3	47.7	88	160
Fuel oil	41 800 MJ/m^3	34.5-206	206	292
Coal	27.6 MJ/kg	145	361.5	361.5

[a] In the BRD, NO_x emission rate for gas-heated residences is 23 to 47 pkg/J; for hard-coal heating, it is 1 kg/1 000 kg of coal.



Source	NO_2 (Mkg)	
Gas	214	
Petroleum	289	
Gasoline		420
Diesel		359
Coal	1 377	
Industrial non-combustion	177	
Waste incineration	4	
BRD Total	3 061	

Figure 3-3. Total estimated oxides of nitrogen emissions from mobile and stationary sources in the BRD, 1970.

Total estimated oxides of nitrogen emissions (NO_2) from stationary installations in the BRD, 1970, are shown in Figure 3-4.

Atmospheric NO can react with oxygen to form nitrogen dioxide (NO_2). The NO_2 removed from the atmosphere by hydrolysis becomes nitric acid, which is precipitated as nitrates in rainfall or in dusts. The residence time of NO_2 in the atmosphere is only a few days.[4] The natural nitrogen cycle of organic growth—decomposition into the atmosphere and return to the soil as a natural fertilizer—produces a worldwide NO_2 emission of about 455 Gkg/yr.[5]

3.1 LARGE-SCALE FOSSIL FUEL COMBUSTION PROCESSES

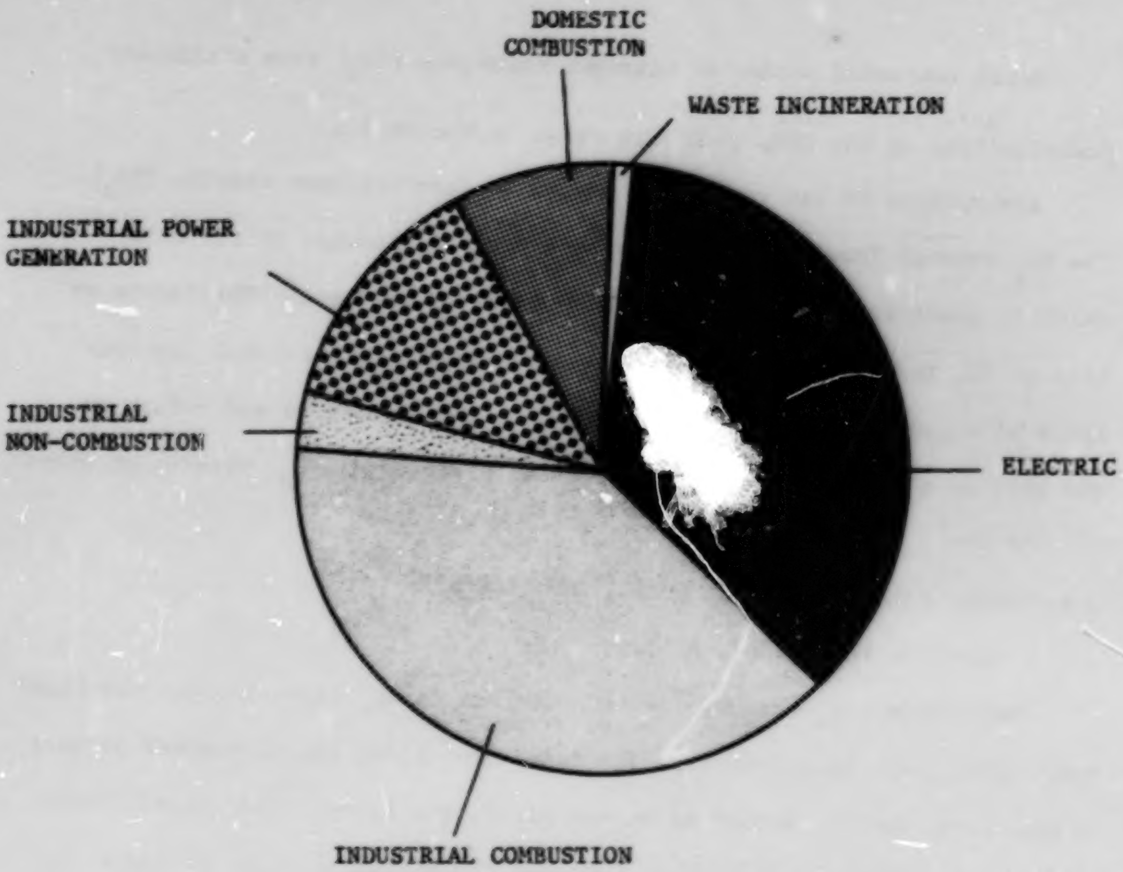
3.1.1 Electric Power Plant Boilers

For combustion sources, the main factors in NO_x formation are the flame temperature, the length of time the combustion gases are maintained at that temperature, and the amount of excess air in the flame. When fossil fuels (gas, fuel, oils, and coal) burn, some of the oxygen (O_2) and nitrogen (N_2) in the air combine:

$$N_2 + O_2 \rightleftarrows 2NO. \qquad (1)$$

Given time, this reaction proceeds to equilibrium. Decomposition of NO is too slow for it to dissociate into oxygen and nitrogen under ordinary reaction conditions; as a result, it persists, or is "frozen," in the flame products that leave the high-temperature zone. Table 3-3 shows the effect on NO formation of small changes in residence time and temperature.

Emissions from power plant boilers fired with fossil fuels are largely determined by the design and operation of the equipment; the type of firing and the spacing and location of burners, particularly in the large boilers, have marked effects (Section 4.1).



Type of installation	NO_2 (Mkg)
Electrical utility	780
Industrial combustion	850
Industrial non-combustion	120
Industrial power generation	320
Domestic combustion	120
Waste incineration	5
BRD Total	2 195

Figure 3-4. Total estimated oxides of nitrogen emissions from stationary installations in the BRD, 1970.

Table 3-3. TIME FOR NO FORMATION IN A GAS CONTAINING 75 PERCENT NITROGEN AND 3 PERCENT OXYGEN[6]

Temperature, K	Time to form 500-ppm of NO, s	NO concentration at equilibrium, ppm
1 580	1 370	550
1 810	16.2	1 380
2 030	1.10	2 600
2 250	0.117	4 150

Table 3-4. STATIONARY RECIPROCATING PISTON ENGINES IN UNITED STATES, 1967

Engine type	Fuel	Percent of total[a]
Full diesel	Liquid fuel oil	15
Dual fuel	Liquid or gas	19
Spark-ignition gas	Gas	66

[a] It is estimated 85 percent of these engines are supercharged;[7] about 1 percent are the precombustion-chamber type.[8]

3.1.2 Stationary Engines

Stationary engines can be either piston engines, further classified in Table 3-4, or gas turbines. Piston engines have an estimated capacity of approximately 52 200 MW--assuming that two-thirds of the engines are gas fired and assuming a fuel consumption rate of 67.5 nkg/J; this estimate, based on distillate fuel oil consumption by "industrial and other" stationary engines,[9] is probably low because many large oil-fueled diesel engines use heavy fuel oil, which would not appear in the distillate fuel figures. Gas turbine engines have an estimated total capacity of 38 000 MW, assuming that 60 percent of the worldwide stationary turbines are in the United States and that 90 percent are fueled with natural gas.

The NO_x emission data for stationary engines are listed in Table 3-5. The data for piston engines are based on experiments using relatively small engines (e.g., 150 kW), and there is some question about extrapolating to larger engines. However, as indicators of the effects of engine variables, the data are considered valid. Data on gas turbine engines are from conventional turbojets. On the basis of these data, the following preliminary observations were made:

1. Turbocharging a piston engine increases NO production.
2. A precombustion-chamber piston engine produces only about one-third as much NO_x as an oil-fired, direct-injection diesel engine.
3. An oil-fired turbojet engine produces about one-tenth as much NO_x as a direct injection diesel engine.

Table 3-6 summarizes data obtained in tests on two large dual-fuel (oil and gas) stationary diesel engines. For the larger engine, the

Table 3-5. ESTIMATED STATIONARY ENGINE DISTRIBUTION IN UNITED STATES, 1969[a]

Type of stationary engine	Super-charged	Fuel	Total power, MW	Reference	Oxides of nitrogen emissions: NO_x, kg/kg fuel	Oxides of nitrogen emissions: NO_x, pkg/J
Reciprocating engine						
Diesel, precomb. chamber	Yes	Oil	522		(0.02)[b]	380[b]
Diesel, precomb. chamber	No	Oil	74	4	0.007-0.010	160-230
Diesel, direct injection	Yes	Oil	10 400	5	0.07	1 630
Diesel, direct injection	No	Oil	1 490	4,5,6,7	0.021-0.047	510-1 110
Gas engine, spark ignited	Yes	Gas	33 500		(0.16)	3 430
Gas engine, spark ignited	No	Gas	6 000	8	0.084	1 710
Gas turbine						
Turbojet	--	Oil	3 700	9	0.008-0.01	40-130
Turbojet	--	Gas	34 300		(0.004)[b]	80[b]

[a] Estimated figures in parentheses are based on assumption that supercharging doubles NO_x emissions.

[b] Estimates are based on assumption that gas will emit the same amount of NO_x as turbo fuel. This may be open to question, and probably penalize the turbojet engine. If the turbine engine responded to gas fuel in the same way as the diesel engine, NO_x emissions would be of the order of 17.2 pkg/J, a very low air pollutant emission level.

Table 3-6. SUMMARY OF SOURCE-SAMPLING TESTS FOR TWO DUAL-FUEL (GAS AND DIESEL) ENGINES

Fuel	Engine 1		Engine 2	
	Diesel No. 2	Natural gas	Diesel No. 2	Natural gas
Airflow, kg/s	4.70	3.90	2.50	2.30
Air/fuel ratio	35.6	31.5	33.0	34.6
Exhaust flow, m^3/s^a	4.20	3.47	2.32	2.14
NO_x, kg/kg fuel	0.074	0.075	0.066	0.038
NO_x, nkg/J	1.73	1.50	1.55	0.76
NO_x, ppm	1 375	1 544	1 251	746
Percent rated load	77		80	
Brake power, kw	2.38		1.38	
Brake mean effective pressure, kN/m^2	724		1 103	
Engine speed, rpm	360		514	

[a] (101 kN/m^2).

brake mean effective pressure (BMEP) and engine speed were lower than for the smaller engine, the air-fuel ratio was higher than those in automotive diesels under similar load conditions, and the particulate emissions were extremely low. The data indicate that slower engines produce higher concentrations of NO_x; that is expected because of the longer residence time of the gases at high temperatures in the engine cylinders.

Emissions of NO_x from a gas turbojet engine are about one-tenth those of a diesel engine. Even by correcting for a difference in thermal efficiency (20 versus 30 percent), a gas turbine emits only about one-sixth of the NO_x emitted by a diesel. Further improvements may be worthy of consideration if costs--not only original investment but also economy of operation, performance, and the like--are not too high.

3.2 SMALL-SCALE COMBUSTION PROCESSES

Estimates of total NO_x produced in the United States by stationary engines given in Table 3-5 indicate that a large fraction of the fossil fuels burned and the NO_x emissions released are associated with small-scale combustion processes for domestic and commercial heating, hot water supply, a wide variety of incinerators, and the burning of solid wastes. Larger users of fuels than the electric utilities but with less intense combustion, these small non-industrial processes contribute significantly to NO_x emissions in residential areas.

3.2.1 Domestic and Commercial Heating

Some 20 percent of the fossil fuels used in the United States for energy production (transportation excluded) is consumed in domestic and commercial heating. Annually, this is 13 709 x 10^{15}J compared to the 17 613 x 10^{15}J consumed for power generation by electric utilities.[10]

Some 28 percent of the fossil fuels in the BRD for energy production (transportation excluded) is consumed in domestic and commercial heating.

In 1970 this was 2.3×10^{18}J compared to the 1.8×10^{18}J consumed for power generation by electric utilities (0.8×10^{18}J consumed for industrial power generation excluded).

Of the 29 million domestic control heating units, about 18 million use gas, about 10.7 million use oil, and only about 0.3 million use coal.[11] These units, together with associated cooking facilities, consume fuel as indicated in Table 3-7; a further breakdown of gas consumption is given in Table 3-8. In the BRD the fuel consumption for space heating and cooking in 1970 is shown in Table 3-9.

The amount of fuel used for domestic appliances (e.g., water heaters, cooking ranges, gas refrigerators, and clothes dryers) remains reasonably constant throughout the year, but in many areas, midwinter requirements for space heating increase to well over 50 percent of the total fossil fuel consumption.

The NO_x contribution of residential space heating is indicated by data on seasonal and diurnal fuel usage from the Continuous Air Monitoring Projects (CAMP) and other sources; the data show a strong correlation between sulfur dioxide (SO_2) emissions in urban areas and the daily and yearly residential heating requirements.[13-15]

Gaseous emissions from domestic units are vented close to the ground, and according to data from CAMP and other studies, chimney gases are poorly dispersed. This means that a given amount of NO_x from this source has a greatly aggravated effect on ambient air, especially under adverse conditions such as stagnation or aerodynamic downlash, compared to the same amount from a tall utility stack. Commercial buildings and apartments presumably show intermediate effects.[15]

Table 3-7. FUEL CONSUMPTION FOR SPACE HEATING AND COOKING IN UNITED STATES, 1966

Fuel type	Quantity	Equivalent heating value,[12] 10^{18}J
Natural gas	163 km^3	6.3
Distillate fuel oil	75 hm^3	3.0
Residual fuel oil	26 hm^3	1.1

Table 3-8. ANNUAL GAS CONSUMPTION FOR DOMESTIC HEATING IN UNITED STATES

Number of customers	Type of use	Avg. heat use, GJ/unit	Total heat use, 10^{18}J
28 800 000	Heating unit (1 and 2 family)	107	3.0
33 000 000	Hot water	31	1.0
38 200 000	Ranges	10	0.4
Total			4.5

Table 3-9. FUEL CONSUMPTION FOR SPACE HEATING AND COOKING IN THE BRD, 1970

Fuel type	Quantity	Equivalent heating value, 10^{15}J
Gas		
Natural gas	1.5 km^3	160
Sewer gas	5.0 km^3	
Fuel oil	36 Gkg	1 510
Coal		
Lignite	210 x 10^{15}J	210
Bituminous	370 x 10^{15}J	370

Unit size and severity of operation have direct bearings on NO_x emissions (Fig. 3-1).[16] Gas-fired domestic furnace with a capacity of 158 000 kJ produces only about 12 percent of the NO_x produced in a large utility boiler of 10.6 TJ from consumption of an equivalent amount of fuel. A similar ratio exists for oil-fired units. Although domestic and commercial heating units consume approximately the same amount of fuel as utility boilers, their NO_x contribution is only about 7 percent of all NO_x in the United States, compared to 44 percent for the utilities.

3.2.2 Incineration and Other Burning

Preliminary results of a survey by the U.S. Public Health Service in 1968 indicate that household, commercial, and industrial solid waste production per capita is about 4.53 kg/day or 326 Gkg/yr. About 172 Gkg/yr (or 2.49 kg/day per capita) is collected for disposal; the remainder is either disposed of on site or handled by the household or establishment itself.[17] An estimated 160 Gkg is burned in the open or in incinerators.[18]

An additional 500 Gkg of agricultural waste, 1 360 Gkg of animal wastes, and 998 Gkg of mineral wastes are generated each year.[17] It is estimated that half of the agricultural wastes is burned annually in the open and that, except for 430 Gkg of coal refuse consumed by fire, no animal or mineral wastes are burned; forest-burning and structural fires consumes about 181 Gkg and 7 Gkg/yr respectively.[18] Waste production in the BRD (1970) is given in Table 3-10.

Incineration and open burning reduce the weight and volume of solid waste. High-temperature incineration with excess air reduces emissions of particulate matter, carbon monoxide, and smog-forming compounds such as aldehydes, hydrocarbons, and organic acids (which typify open burning), but it increases NO_x emissions.

Table 3-10. WASTE PRODUCTION IN THE BRD, 1970[19] (Gkg)

Source	Quantity
Household	16[a]
Commercial	4
Industrial	2
Building refuse	5
Mining and steel industry	20
Settle tank mud	18
Automobile wrecks	1
Agricultural waste	190
Total	256

[a] About 20% incinerated.

Table 3-11. ESTIMATED UNITED STATES EMISSIONS FROM INCINERATION AND OTHER BURNING, 1968[18]

Source	Quantity, Gkg/yr	NO_x emission, Mkg/yr
On-site incineration	52	63
Municipal incineration	15	17
Conical burner incineration	24	16
Open burning	70	408
Agricultural burning	250	254
Controlled forest burning	69	363
Forest wildfires	132	726
Structural wildfires	1	21
Coal refuse fires	44	172
Total	657	2 040

Estimated NO_x emissions from incineration and other burning are shown in Table 3-11. NO_x from incinerator flue gases are 50 to 80 ppm.[20] Open burning produces 8 to 130 ppm.[21] Solid wastes quantities are difficult to measure, particularly for open burning; the emission factor given in Table 3-11, however, appears high, since radiation to the sky cools the exposed flame and produces less NO_x emissions than a flame in a closed system (Section 5).

3.3 INDUSTRIAL AND CHEMICAL PROCESSES

For a number of industries, NO_x air pollution problems are minor compared to the more serious problems of smoke, particulates, sulfur dioxide, or organic chemical wastes. Several large industries, such as nonferrous mineral producers or pulp and paper mills, have problems with sulfur dioxide, but no particular concern with NO_x. Other industries, which emit only a small percentage of the national total, can cause dangerous local concentrations of NO_x if uncontrolled. The chemical industry, more than any other, has studied the problem of NO_x emissions because those emissions represent the loss of a valuable raw material. This is especially true in the manufacture and the industrial uses of nitric acid.

The NO_x released in vent gases from the manufacture and uses of nitric acid are quite different in terms of concentration, total amount, and the ratio of NO_2 to NO from those emitted from combustion flue gases. Vent gas is released when it is either too impure to recycle or too low in NO_x content for economic recovery (in nitric acid manufacture, about 0.1 to 0.3 percent NO_x; in organic nitrations, about 1 percent NO_x).

Chemical manufacturing processes emit about 1 percent of all NO_x from manmade sources in the United States and are problems only in local areas.

They are most serious in military ordnance works which manufacture and use large volumes of nitric acid in organic nitrations; for example, in a single plant like the Volunteer Ordnance Works, emissions of NO_x can equal those from all U.S. nonmilitary uses of nitric acid.

Brownish plumes are caused by highly concentrated gases with high NO_2-NO ratios. If the NO_2 concentration in ppm multiplied by the stack diameter in mm exceeds 60 000, the plume will be brown.[22] This means that the threshold of visibility for a 50.8-mm-diameter stack is about 1 200 ppm NO_2 and for a 305-mm-diameter stack, 200 ppm NO_2.

3.3.1 Nitric Acid Manufacture

All nitric acid manufactured in the United States is made by the catalytic oxidation of ammonia. Air (O_2) and ammonia (NH_3) are preheated, mixed, and passed over a catalyst, usually platinum-rhodium:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \ . \qquad (2)$$

When the steam is cooled to 310 K or less, the NO reacts with more oxygen to form the brown, pungent NO_2 and its liquid dimer, nitrogen tetroxide (N_2O_4):

$$2NO + O_2 \rightarrow 2NO_2 \rightleftarrows N_2O_4 \ . \qquad (3)$$

Then, the liquid and gas enter an absorber, where one or both react with water to form NO and nitric acid (HNO_3):

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \ . \qquad (4)$$

Air entering the bottom strips NO_2 from the acid product and supplies oxygen for reoxidizing the NO. The formation of 1 mole of NO for each 2 moles of HNO_3 makes it necessary to reoxidize NO after each absorption stage to prevent the gas from rising in the absorber and limiting the level of recovery that can be economically achieved. Acid is withdrawn from the bottom of the tower in concentrations of 55 to 65 percent.

Currently, pressures of 552 to 827 kN/m^2 are used for the oxidation and absorption. Before corrosion-resistant materials were developed, when the operations were carried out at essentially atmospheric pressure, the resulting low absorption and NO oxidation rates required much more volume and several large towers in series. Today, low-pressure units comprise less than 5 percent of the U.S. nitric acid plant capacity; over 90 percent is the more economical pressure type.[23] In the BRD all new plants are the more economical pressure type. A typical flow plan is shown in Fig. 3-5. In order to protect the reheater from acid mist a packed fiber bed may be installed behind the absorption tower.

Packed fiber beds are also used as platinum filters (more than 90% efficiency). Combination pressure plants carry out the ammonia oxidation at low pressure and absorption at high pressure; intermediate-pressure plants carry out both operations at intermediate pressures.

For most uses, the 55 to 65 percent nitric acid is satisfactory; for some, higher strength is required. These requirements are met by concentrating the lower strength acids. Figure 3-6 illustrates a nitric acid concentration unit using extractive distillation with sulfuric acid: a mixture of strong sulfuric acid and 55 to 65 percent nitric acid introduced at the top of a packed column flows downward, the vapors of 98 percent nitric acid and small amounts of NO_x and oxygen (from dissociation of the acid) pass from the top of the column to a bleacher and a condenser. The condensed nitric acid and the separated NO_x and oxygen pass to an absorber column for conversion to and recovery of the acid, and the diluted sulfuric

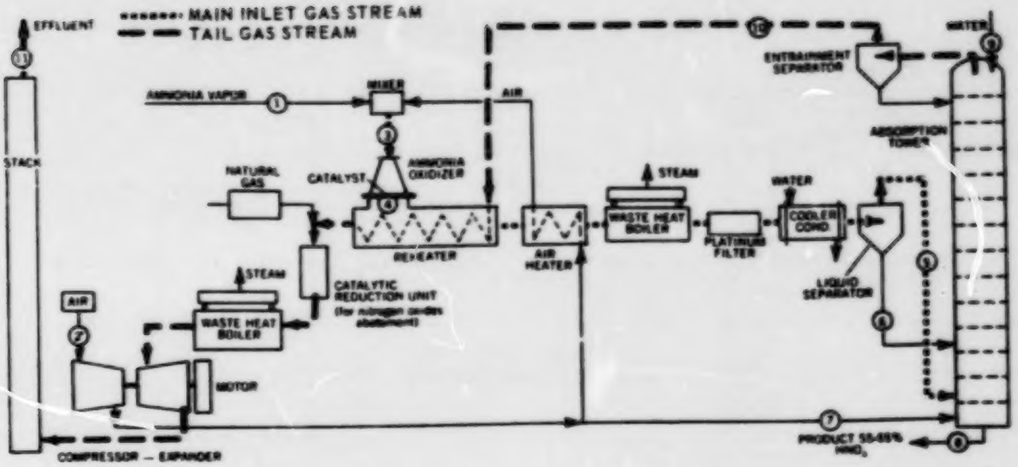

MAIN INLET GAS STREAM
TAIL GAS STREAM
EFFLUENT
11
STACK
AMMONIA VAPOR
1
MIXER
AIR
3
AMMONIA OXIDIZER
CATALYST
4
NATURAL GAS
REHEATER
CATALYTIC REDUCTION UNIT
(for nitrogen oxides abatement)
STEAM
WASTE HEAT BOILER
AIR
2
MOTOR
COMPRESSOR — EXPANDER
AIR HEATER
STEAM
WASTE HEAT BOILER
PLATINUM FILTER
WATER
COOLER COND
LIQUID SEPARATOR
5
6
7
PRODUCT 55-65% HNO$_3$
8
10
ENTRAINMENT SEPARATOR
WATER
9
ABSORPTION TOWER

Figure 3-5. Flow diagram of a typical 109 000 kg/day nitric acid plant utilizing the pressure process.

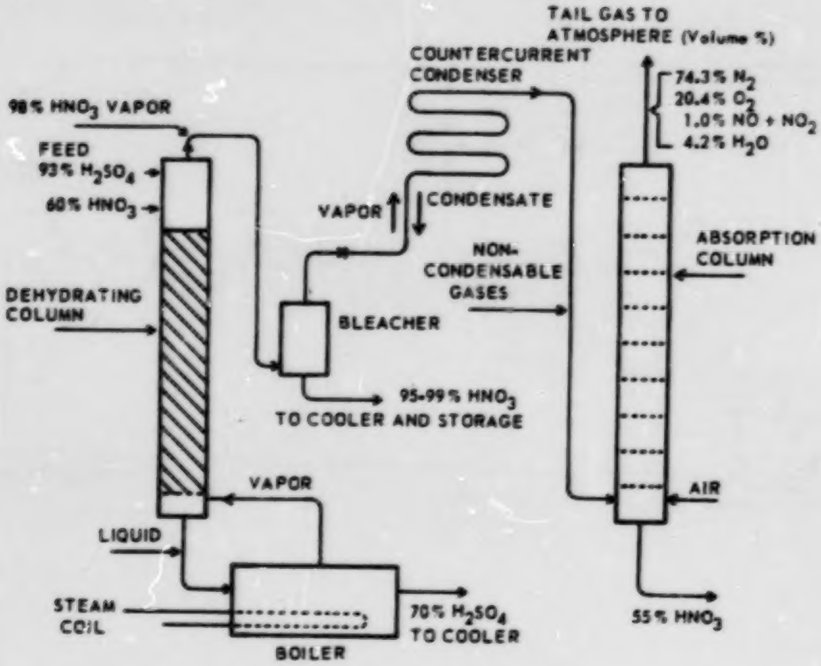

TAIL GAS TO ATMOSPHERE (Volume %)
74.3% N_2
20.4% O_2
1.0% NO + NO_2
4.2% H_2O
COUNTERCURRENT CONDENSER
98% HNO_3 VAPOR
FEED
93% H_2SO_4
60% HNO_3
VAPOR
CONDENSATE
ABSORPTION COLUMN
NON-CONDENSABLE GASES
DEHYDRATING COLUMN
BLEACHER
95-99% HNO_3 TO COOLER AND STORAGE
VAPOR
AIR
LIQUID
STEAM COIL
70% H_2SO_4 TO COOLER
BOILER
55% HNO_3

Figure 3-6. Nitric acid concentrating unit.

acid withdrawn from the bottom of the dehydrating tower is either concentrated further or used for other purposes. The system usually operates at atmospheric pressure.

The Hoko process,[24] unlike other processes, makes concentrated (98 to 99 percent) nitric acid directly, but it is seldom used in the United States, where concentrations of 55 to 65 percent are usually satisfactory. In the Hoko process, ammonia is burned with air or oxygen at atmospheric pressure; the combustion gases are rapidly cooled to about 300 K in order to remove the water as dilute nitric acid (1 to 2 percent). The gases are then compressed, and the NO is oxidized to NO_2, which is absorbed in cold concentrated nitric acid. The gas from the absorber is scrubbed with weak acid to remove HNO_3, and the absorber liquid (N_2O_4-HNO_3) is mixed with water, autoclaved, and oxidized with pure oxygen to make 98 or 99 percent nitric acid. The NO_x in the tail gas is 0.05 percent by volume.[25] Disposal of the weak acid formed by condensing the ammonia oxidation vapors is a problem.

Rough estimates of total industrial acid requirements and resulting NO_x emissions for the United States in 1967 are shown in Table 3-12; not included are requirements and emissions from nitric acid concentration operations for producing military explosives. Emissions of NO_x from nitric acid manufacturing were estimated at 132 Mkg/yr for 1967--about 1 percent of the total, or 2 percent of the pollution from all stationary sources. This estimate was based on the production of 5.55 Gkg of nitric acid[26] and on an average NO_x emission factor of 22.5 kg/1 000 kg of acid.[23] About 700 Mkg of nitric acid were produced in 1969 in the BRD. The NO_x emissions (calculated as NO_2) are reported as 35 Mkg for 1969--about 1 percent of the total, or 2 percent of the pollution from all stationary sources.[27]

In 1980 the production will be about 1.3 Gkg of nitric acid and the NO_x emission (calculated as NO_2) about 30.6 Mkg. Without controls, a 726 000 kg/day-plant (the largest currently built) would emit about 680 kg/hr.

The major emission source is absorber tail gas. Minor sources are nitric acid concentration and the filling of storage tanks and shipping containers. Tail gas contains about 0.3 volume-percent (300 ppm) of NO_x, with about equal concentrations of NO and NO_2. About 2.49 kg/1 000 kg of nitric acid is emitted in the absorber gas from concentration units. Typical NO_x concentration is about 1 percent,[23] reflecting operation at essentially atmospheric pressure. High NO_x levels may be caused by insufficient air supply, high temperatures in the absorber tower, low pressure, the production of acid at strengths above design, and internal leaks which permit NO_x to enter the tail-gas streams. Careful control and good maintenance are required to minimize NO_x content of tail gas.

3.3.2 Nitric Acid Uses

Approximately 75 percent of the nitric acid produced in the United States is consumed in making ammonium nitrate. Adipic acid manufacture consumes about 9 percent. No other single outlet consumes more than about 4 percent. Estimated quantities consumed in each important use are listed in Table 3-13; these include metal pickling and etching, nitrations and oxidations of organic compounds, and production of metallic nitrates.

3.3.2.1 Ammonium Nitrate Manufacture--Ammonium nitrate (NH_4NO_3) is produced by the direct neutralization of nitric acid (HNO_3) with ammonia (HN_3)

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 \ . \qquad (5)$$

Table 3-12. ESTIMATES OF STRONG ACID REQUIREMENTS AND NO_x EMISSIONS FROM CONCENTRATION OPERATIONS IN THE UNITED STATES, 1967

Use	Nitric acid requirements			Emission
	Total HNO_3, Mkg	Strong acid, %	Strong acid, Mkg/yr	NO_x, 1 000 kg/yr
Nitrobenzene	82	72	59	147
Toluene diisocyanate	68	51	34.5	86
Commercial explosives	35	100	34.5	86
Total	184		128	319

Table 3-13. ESTIMATED NITRIC ACID CONSUMPTION IN UNITED STATES, 1967[26]

Use	Quantity, Mkg
Ammonium nitrate	4 110
Adipic acid	500
Terephthalic acid	90
Nitrobenzene	80
Toluene diisocyanate	60
Commercial explosives (e.g., NH_4NO_3)	30
Fertilizers (e.g., NH_4NO_3)	130
Other uses	510
Total	5 510

About 735 kg of nitric acid (100 percent equivalent) and 190 to 204 kg of anhydrous ammonia are required to make 907 kg of ammonium nitrate. Typical feed contains 55 to 60 percent nitric acid, which produces an aqueous solution of ammonium nitrate. Usually, the heat of reaction evaporates part of the water and produces a solution of 83 to 86 percent ammonium nitrate for use as a liquid fertilizer. Further evaporation to a solid may be accomplished by falling-film evaporation,[28] by disk-spraying,[29] or by evaporation to dryness in a raked shallow open pan (graining),[29] "prilling"--a process in which molten ammonium nitrate flows downward through a tower in a rising stream of air which cools the melt and produces pellets or prills.[30]

In 1967, production of 5.1 Gkg of ammonium nitrate[26] required about 4.1 Gkg of nitric acid. About 635 Mkg to 725 Mkg of the ammonium nitrate were used in explosives, and most of the remainder was either used in direct applications or in mixed fertilizers.[31]

The most likely source of nitric acid emissions is neutralization. However, because the vapor pressure of ammonia is much higher than that of the acid, the release of acid fumes or NO_x is believed to be negligible,[32] especially since a slight excess of ammonia is used to reduce product decomposition. About 1.1 Gkg (N) nitrogenous fertilizer (1970) produced about 0.45 Mkg of NO_2.[33]

3.3.2.2 Organic Oxidations--Nitric acid is used as an oxidizing agent in the commercial preparation of adipic acid, terephthalic acid, and other organic compounds containing oxygen. The effective reagent is probably NO_2, a very strong oxidizing agent.

Adipic acid ($COOH \cdot (CH_2)_4 \cdot COOH$), a dibasic acid used in the manufacture of synthetic fibers, is made in the United States in a two-step continuous operation (Fig. 3-7). The first step is the catalytic oxidation of cyclohexane by air to a mixture of cyclohexanol and cyclohexanone; the second is the catalytic oxidation of the mixture by 45 to 55 percent nitric acid. The product is purified by crystallization.[34] In the second step, the nitric acid requirement is 1.46 kg/kg of adipic acid, of which 0.19 kg is potentially recoverable NO_x (NO and NO_2) and 0.46 kg is unrecoverable NO_2.[35]

Terephthalic acid, an intermediate in the production of polyethylene terephthalate, is used in polyester, films, and other products. This acid can be produced in a single reactor by the two-step oxidation of paraxylene by nitric acid (Fig. 3-8): the first step yields primarily N_2O, the second mostly NO in the off-gas.[36] The nitric acid requirement is estimated to be 1.33 kg/kg of terephthalic acid, of which 0.34 kg is potentially recoverable NO and 0.26 kg is unrecoverable N_2O. According to the production of adipic acid and terephthalic acid, an emission of 1.53 Mkg (NO_2) was estimated.

In 1967, total terephthalic acid production was about 358 Mkg, of which an estimated 136 Mkg was made by nitric acid oxidation. Adipic acid production was about 490 Mkg[37] all of which is believed to be from the nitric acid oxidation of cyclohexanol-cyclohexanone. Nitric acid is used for the oxidation of other organic compounds, but none approach terephthalic or adipic acid in product volume.

The offgases leaving manufacturing operations using nitric acid as an oxidizing agent may contain as much as 50 percent NO_x before acid recovery.[35,36] Absorption systems recover an estimated 98 to 99 percent of the NO_x as nitric acid. (NO_2, a principal compound in the off-gas, is not oxidized to NO_x in the atmosphere and is considered harmless.) NO_x emissions from the production of terephthalic and adipic acids are estimated

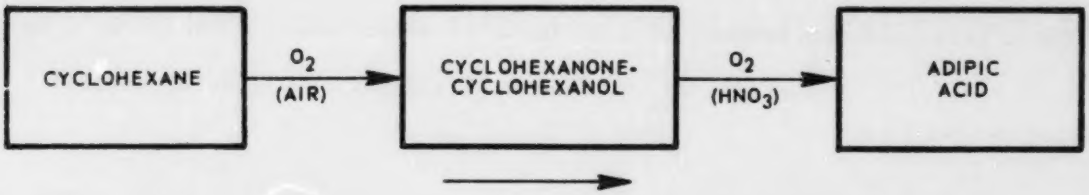

CYCLOHEXANE
O_2
(AIR)
CYCLOHEXANONE-
CYCLOHEXANOL
O_2
(HNO_3)
ADIPIC
ACID

Figure 3-7. Adipic acid synthesis.

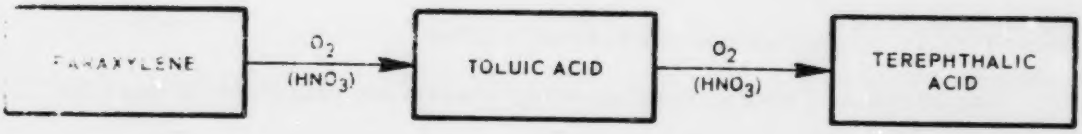

PARAXYLENE
O_2
(HNO_3)
TOLUIC ACID
O_2
(HNO_3)
TEREPHTHALIC
ACID

Figure 3-8. Terephthalic acid synthesis.

at 7.60 Mkg based on emission factors.[38] These emissions amount to 0.07 percent of the total from all stationary sources, or 0.04 percent from all U.S. sources.

3.3.2.3 Organic Nitrations--Nitration is the treating of organic compounds (RH or ROH) with nitric acid or NO_2 to produce nitro compounds (RNO_2) or nitrates ($RONO_2$). The following equations illustrate the two most common types of reaction:

$$RH + HNO_3 \rightarrow RNO_2 + H_2O \; ; \tag{6}$$

$$ROH + HNO_3 \rightarrow RONO_2 + H_2O \; . \tag{7}$$

Products of the first reaction (C-nitration) are compounds such as nitrobenzene, nitrotoluenes, and nitromethane; products of the second (O-nitration) are nitroglycerine (or glyceryl trinitrate) and nitrocellulose. Nitrobenzene and dinitrotoluenes (from C-nitrations) are produced in large volumes as chemical intermediates. Explosives such as trinitrotoluene (TNT), nitroglycerin, and nitrocellulose (from O-nitration) are produced in significant but smaller volumes.

The nitrating agent used commercially is either nitric acid, a mixture of nitric and sulfuric acids, or NO_2. The mixture of acids is most frequently used. When nitric acid alone is used, the weak spent acid is recovered in an absorption tower and thus replaces some of the water fed as absorbent. When the mixture is used, the sulfuric acid promotes formation of NO_2^+ ions, absorbs the water from the reaction, and the spent acid is recovered in a system similar to that shown in Fig. 3-9.[39] Mixed acid enters the top of the denitrating tower, in which superheated steam rising from the bottom drives off the spent nitric acid and the NO_x. The nitric acid is liquified in a condenser and withdrawn to storage, the uncondensed

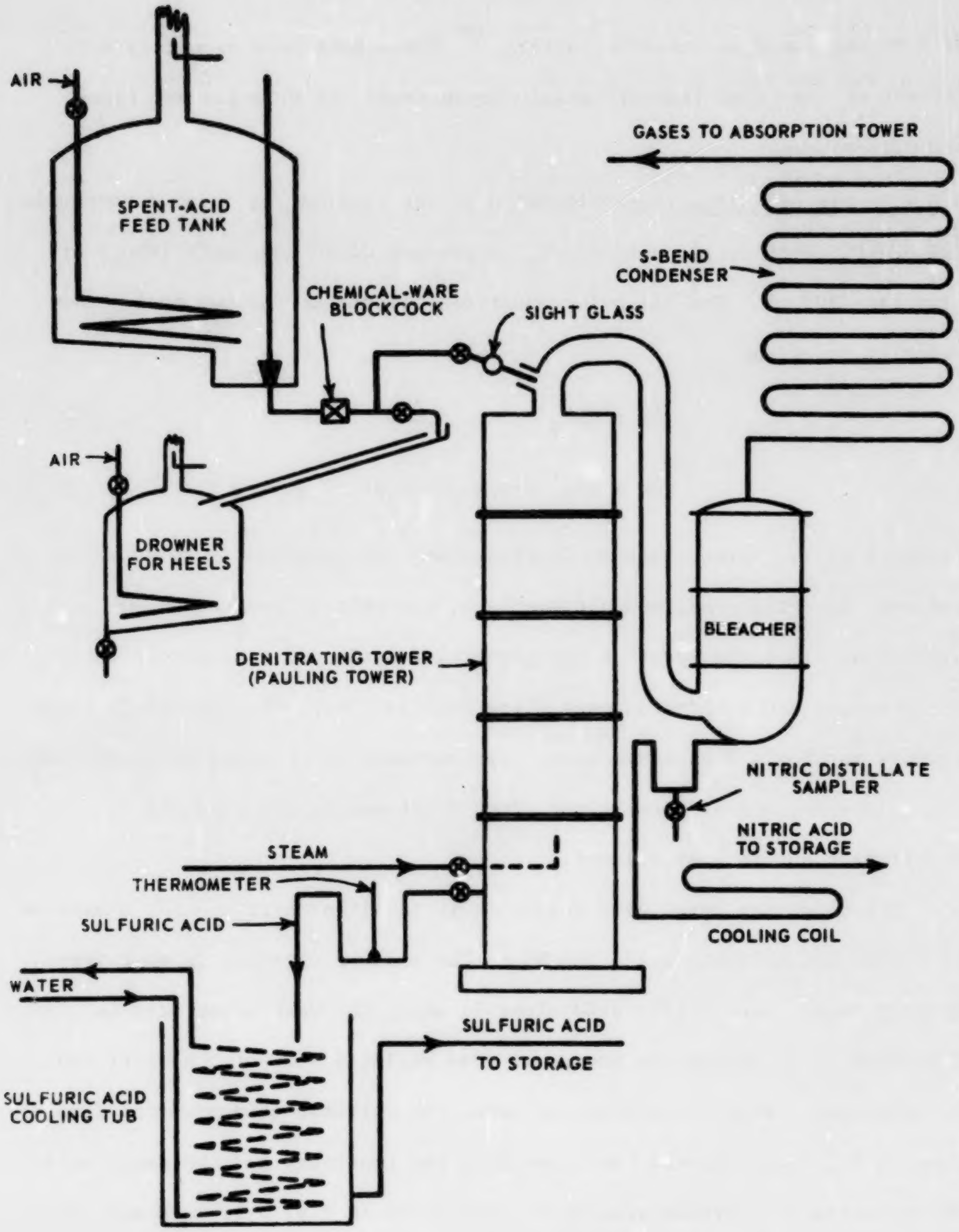

AIR
SPENT-ACID FEED TANK
CHEMICAL-WARE BLOCKCOCK
SIGHT GLASS
GASES TO ABSORPTION TOWER
S-BEND CONDENSER
AIR
DROWNER FOR HEELS
BLEACHER
DENITRATING TOWER (PAULING TOWER)
NITRIC DISTILLATE SAMPLER
NITRIC ACID TO STORAGE
STEAM
THERMOMETER
SULFURIC ACID
COOLING COIL
WATER
SULFURIC ACID TO STORAGE
SULFURIC ACID COOLING TUB

Figure 3-9. Recovery of spent acid.[39]

gases are sent to an absorption tower, and the weak sulfuric acid is withdrawn from the bottom of the denitrator and either concentrated or disposed of.

Nitration may be either a batch or continuous process. The trend is toward continuous, since control is more easily maintained, equipment is smaller, system holdup is less, and hazards are fewer; however, a multiplicity of specialty products (e.g., dyes and drugs) produced in small volumes will continue to be manufactured by batch nitrations.

A batch nitration reactor is usually a covered vessel with stirring facilities, cooling coils or jackets, a sloped bottom for withdrawing the product from the lowest point, and a large tank containing water (drowning tank) so that explosive products can be discharged promptly and "drowned" in case of abnormal conditions. From the reactor, the contents are transferred to a separator. The product is washed, neutralized, and purified; and the spent acids are processed for recovery. Figure 3-10 illustrates a batch nitration process for manufacturing nitroglycerin.[39]

Two widely employed continuous processes are the Biazzi process (Fig. 3-11) and the Schmid-Meissner process (Fig. 3-12).[39] The Biazzi uses impellers, and the Schmid-Meissner uses compressed air for agitation during washing and neutralizing. Both types of equipment can be used for nitrating in general. Two other processes are the Injector process of the "Nitroglycerin AB", Stockholm (13-16% nitric acid, 73-76% Sulfuric acid, 10-12% water, 2% nitroglycerin and other organic compounds), and the technology of the Hercules Powder Comp. (22.7% nitric acid, 66.3% sulfuric acid, 9.2% water and 1.8% organic compounds).

Nitrobenzene is manufactured in both continuous and batch nitration plants. Both use 53 to 60 percent sulfuric acid, 32 to 39 percent nitric

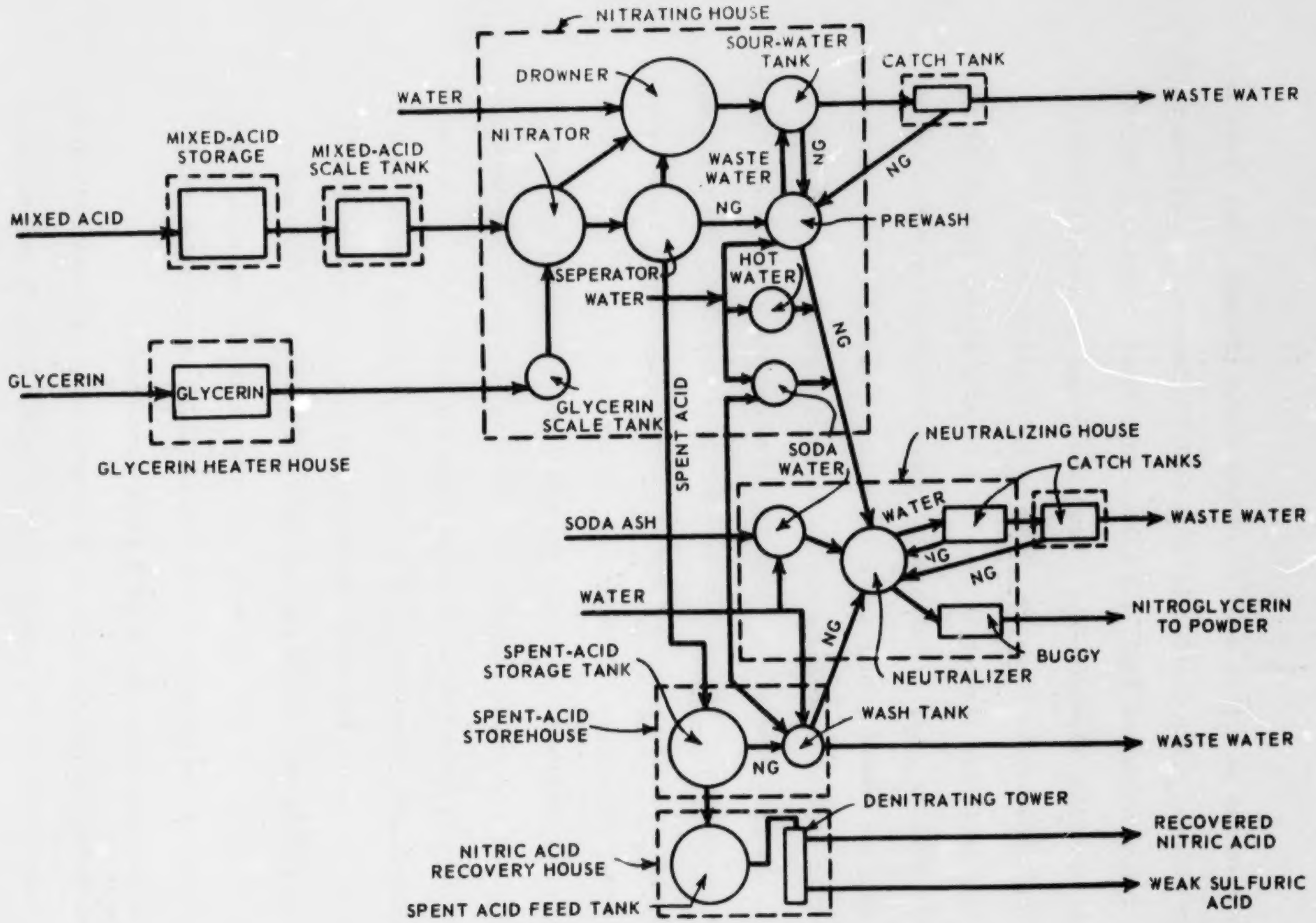

NITRATING HOUSE
MIXED-ACID STORAGE
MIXED-ACID SCALE TANK
MIXED ACID
WATER
DROWNER
NITRATOR
SOUR-WATER TANK
CATCH TANK
WASTE WATER
WASTE WATER
NG
NG
NG
PREWASH
SEPERATOR
HOT WATER
WATER
NG
GLYCERIN
GLYCERIN
GLYCERIN SCALE TANK
GLYCERIN HEATER HOUSE
SPENT ACID
SODA WATER
NEUTRALIZING HOUSE
CATCH TANKS
SODA ASH
WATER
WASTE WATER
NG
NG
WATER
NITROGLYCERIN TO POWDER
BUGGY
NG
NEUTRALIZER
SPENT-ACID STORAGE TANK
SPENT-ACID STOREHOUSE
WASH TANK
NG
WASTE WATER
DENITRATING TOWER
NITRIC ACID RECOVERY HOUSE
SPENT ACID FEED TANK
RECOVERED NITRIC ACID
WEAK SULFURIC ACID

Figure 3-10. Batch process for the manufacture of nitroglycerin (NG).[39]

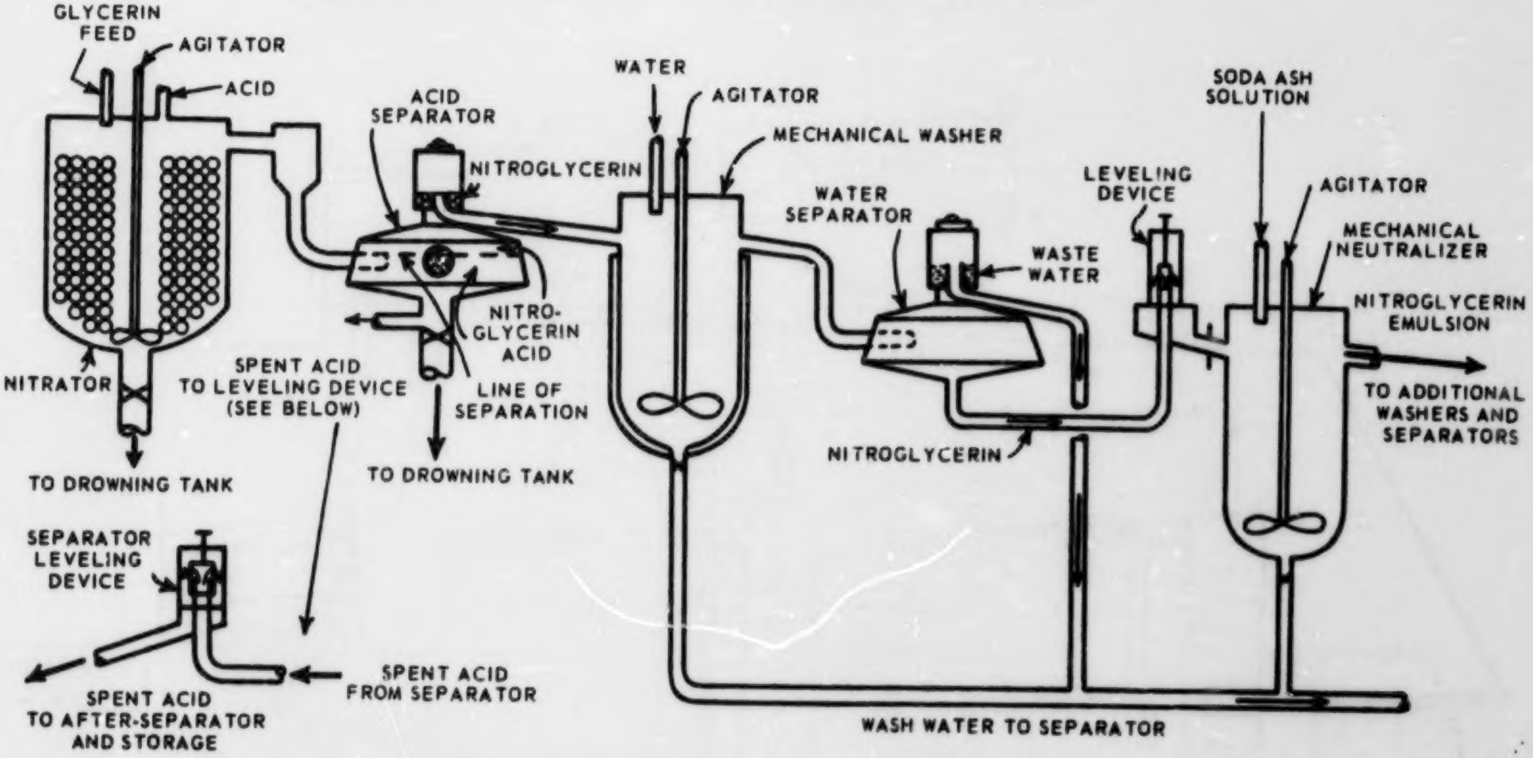

GLYCERIN FEED
AGITATOR
ACID
NITRATOR
TO DROWNING TANK
ACID SEPARATOR
NITROGLYCERIN
NITRO-GLYCERIN
ACID
LINE OF SEPARATION
SPENT ACID TO LEVELING DEVICE (SEE BELOW)
TO DROWNING TANK
SEPARATOR LEVELING DEVICE
SPENT ACID FROM SEPARATOR
SPENT ACID TO AFTER-SEPARATOR AND STORAGE
WATER
AGITATOR
MECHANICAL WASHER
WATER SEPARATOR
WASTE WATER
NITROGLYCERIN
LEVELING DEVICE
SODA ASH SOLUTION
AGITATOR
MECHANICAL NEUTRALIZER
NITROGLYCERIN EMULSION
TO ADDITIONAL WASHERS AND SEPARATORS
WASH WATER TO SEPARATOR

Figure 3-11. Biazzi continuous-nitration plant.[39]

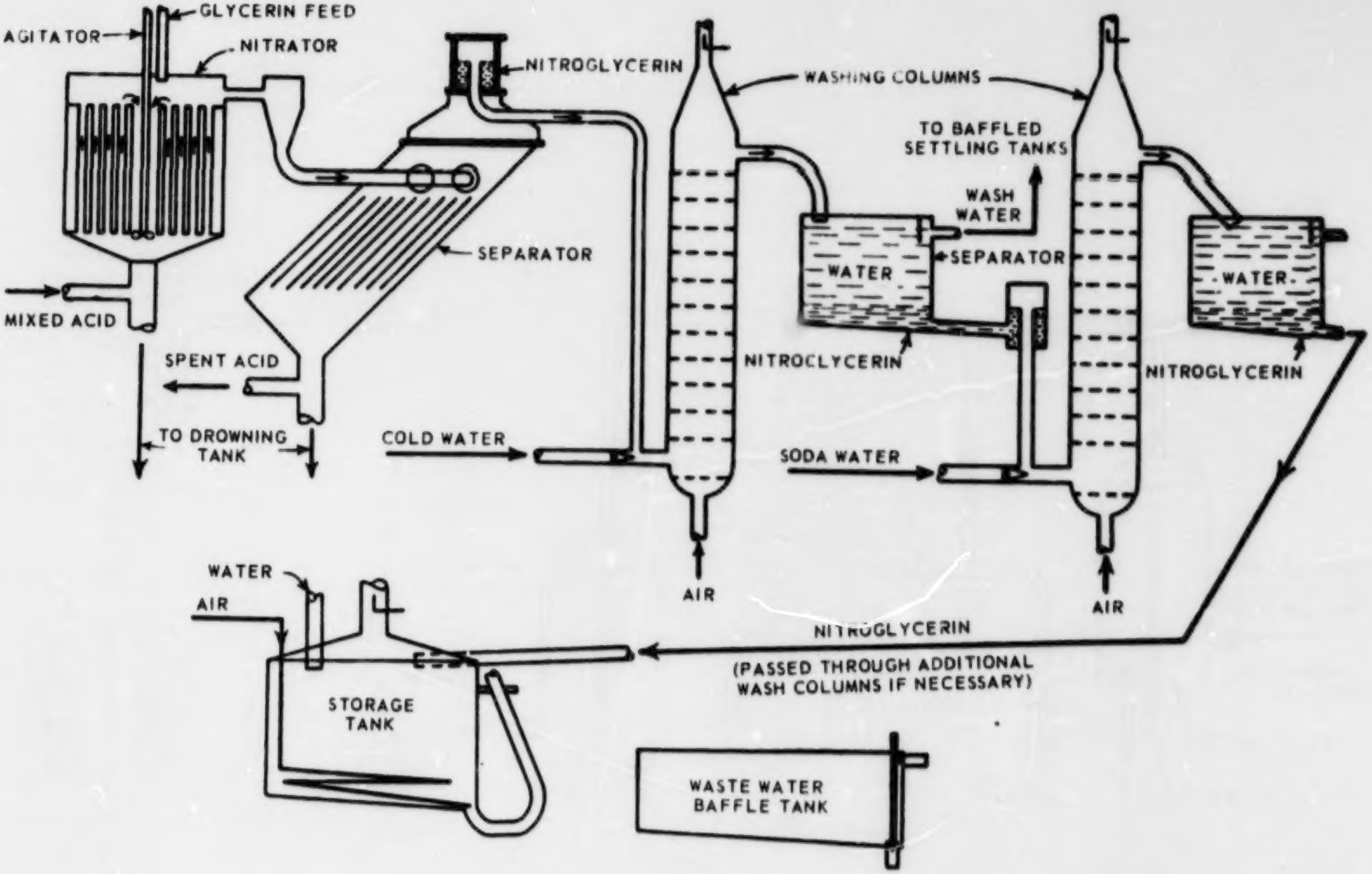

AGITATOR
GLYCERIN FEED
NITRATOR
MIXED ACID
SPENT ACID
TO DROWNING TANK
SEPARATOR
NITROGLYCERIN
COLD WATER
WASHING COLUMNS
AIR
TO BAFFLED SETTLING TANKS
WASH WATER
WATER
SEPARATOR
NITROCLYCERIN
SODA WATER
AIR
WATER
NITROGLYCERIN
NITROGLYCERIN
(PASSED THROUGH ADDITIONAL WASH COLUMNS IF NECESSARY)
WATER
AIR
STORAGE TANK
WASTE WATER BAFFLE TANK

Figure 3-12. Schmid-Meissner continuous-nitration plant.[39]

acid, and 8 percent water. Yields are 95 to 99 percent of theoretical.[40] The main use of nitrobenzene is in the manufacture of aniline, but it is also used as a solvent. From its 1967 production of 154 Mkg and the nitric acid requirements of approximately 0.53 kg/kg of nitrobenzene,[40] nitric acid for nitrobenzene synthesis was estimated at 81.6 Mkg.

Dinitrotoluene is manufactured in two stages in both continuous and batch units. The first, the nitration of toluene to mononitrotoluene, requires 28 to 32 percent nitric acid, 52 to 56 percent sulfuric acid, 12 to 20 percent water, and equipment sized to handle up to 11.4 m^3 for batch processing at 298 to 313 K. Yields of 96 percent are typical.[41] The second step, the production of dinitrotoluene, requires more severe conditions--stronger acid (28 to 34 percent nitric acid and 60 to 64 percent sulfuric acid), less water (5 to 8 percent), and higher temperatures (360 K) after all the acid has been added. Dinitrotoluene yields from mononitrotoluene are about 96 percent of theoretical.[41] The principal use of dinitrotoluene is in making toluene diisocyanate (TDI), usually supplied as mixtures of the 2,4 and 2,6 isomers, used in polyurethane plastics. In 1967, production of of 90.6 Mkg of TDI required 68 Mkg of nitric acid, estimated on the basis of 0.74 kg/kg of TDI.

Sources of NO_x in organic nitrations are the nitration reactor, the denitrator, and auxiliary equipment such as nitric acid concentrators, nitric acid plants, and nitric acid storage tanks. Severe conditions required to process compounds that are difficult to nitrate, such as dinitrotoluene, cause more oxidation and thus more NO_x to be formed. Nitration reactions per se do not generate NO_x emissions; these emissions are formed in side reactions involving the oxidation of organic materials.

For continuous nitrations, 0.06 to 0.12 kg/1000 kg of nitric acid, with a mean of 0.09 kg/1 000 kg have been reported.[42] Emissions were 7 kg/1 000 kg from manufacturing specialty products in small batch operations. With 0.09 and 7 kg/1 000 kg as lower and upper limits, the NO_x emissions in 1967 would range as indicated in Table 3-14. At worst, NO_x emissions from nitrobenzene and dinitrotoluene syntheses are small, but may present local nuisance problems. Since the upper limit represents specialty batch operations on a small scale, the actual emissions are probably much lower than these estimates suggest.

3.3.2.4 Explosives: Manufacture and Use--Nitric acid is consumed in the production of commercial and military explosives. Of the United States commercial explosives, ammonium nitrate (AN) is most widely used because it is the least costly and it is low in relative hazard; nitroglycerin (NG) and trinitrotoluene (TNT) are less widely used. By weight, U.S. commercial explosives consist of over 80 percent ammonium nitrate and 10 percent nitro organic compounds. Ingredients (Table 3-15) were estimated from statistics of the United States Bureau of Mines.[46] Based on the United States 1967 production of 9.07 Mkg of TNT and 25.4 Mkg of NG (Table 3-15), the consumption of nitric acid in the manufacture of commercial explosives, other than AN, is estimated at 34.5 Mkg. The manufacture of AN was discussed in Section 3.3.3.1. The manufacture of TNT is included under military explosives. NG is manufactured in one stage in both batch and continuous units using mixed acids--usually 45 to 50 percent nitric acid and 50 to 55 percent sulfuric acid. Nitric acid consumption for both NG and TNT is about 1 kg/kg of product.[41,47]

Production and consumption data for military explosives are classified; however, several important ingredients are known: penterythritol

Table 3-14. ESTIMATED NO_x EMISSIONS FROM ORGANIC NITRATIONS IN UNTED STATES, 1967

Product	Estimated acid consumption, Mkg/yr	NO_x, 1 000 kg/yr	
		Lower limit	Upper limit
Nitrobenzene	82	7	572
Dinitrotoluene	68	6	481

Table 3-15. INGREDIENTS IN UNITED STATES INDUSTRIAL EXPLOSIVES, 1967

Ingredient	Quantity, Mkg
Ammonium nitrate	
Processed and unprocessed	583
In permissibles[a]	21
In other high explosives[a]	48
In other blasting agents[a]	69
Total	721
Fuel oil, carbonaceous material, and other nonexplosive ingredients[45]	109
Nitroglycerin[45]	25
TNT[45]	9
Total	864

[a] Ammonium nitrate estimated at 65 percent of permissible, 35 percent of other high explosives, and 60 percent of water gels and slurries and rigidly cartridged blasting agents.[43,44]

tetranitrate (PETN), cyclotrimethylene-trinitramine (RDX), trinitrophenylmethylnitramine (tetryl), and TNT. Nitration is an essential step in the manufacture of each; methods of manufacture are detailed by Urbanski.[41] The structures of PETN, RDX, and tetryl are shown in Fig. 3-13. PETN is commonly incorporated into molten TNT to form pentolites. RDX is either used in a mixture with TNT or compounded with mineral jelly to form a plastic explosive. Tetryl is most often used as a primer for less sensitive explosives.

To be used as a military explosive, TNT (symmetrical trinitrotoluene) is manufactured in batch and continuous processes. Addition of each nitro group to the toluene molecule becomes successively more difficult and requires more severe conditions; therefore, it is normal to introduce strong mixed acids at one end and toluene at the other in a multistage operation. As illustrated in Fig. 3-14, the spent acid leaving one stage is fortified with fresh nitric acid before entering the next. As shown in Fig. 3-14, the spent acid from the final stage is denitrated, nitric acid recovered from the denitrator, overhead is recycled, and the noncondensable gas is sent to an absorption tower to recover NO_x and nitric acid. TNT is purified by washing with sodium sulfite (Sellite), which reacts rapidly with the principal impurities (asymmetrical trinitrotoluenes) to form dinitrotoluene sulfonates, soluble in the wash water. The wastewater, called "redwater" because of the deep red color imparted by the nitro compounds, is disposed of by evaporation, the residue by incineration.[41] Operating conditions for nitrating dinitrotoluene to trinitrotoluene are severe--anhydrous mixed acid and 373 K or higher. Yields are limited to 82 to 90 percent of theoretical by oxidation reactions which generate carbon oxides and NO_x.[41] It is, therefore, essential to treat the reactor offgas as well as the

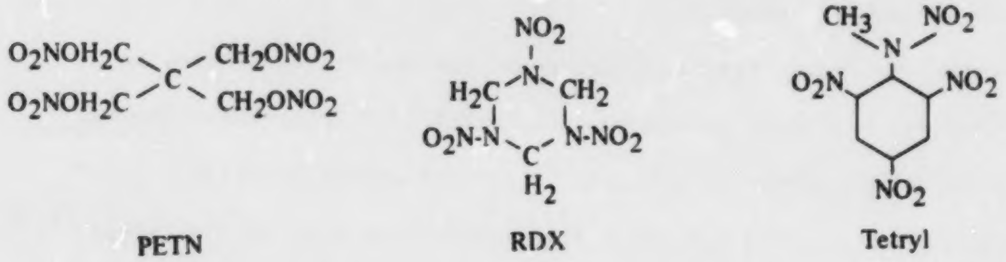

PETN
RDX
Tetryl

Figure 3-13. Structure of PETN, RDX, and tetryl.

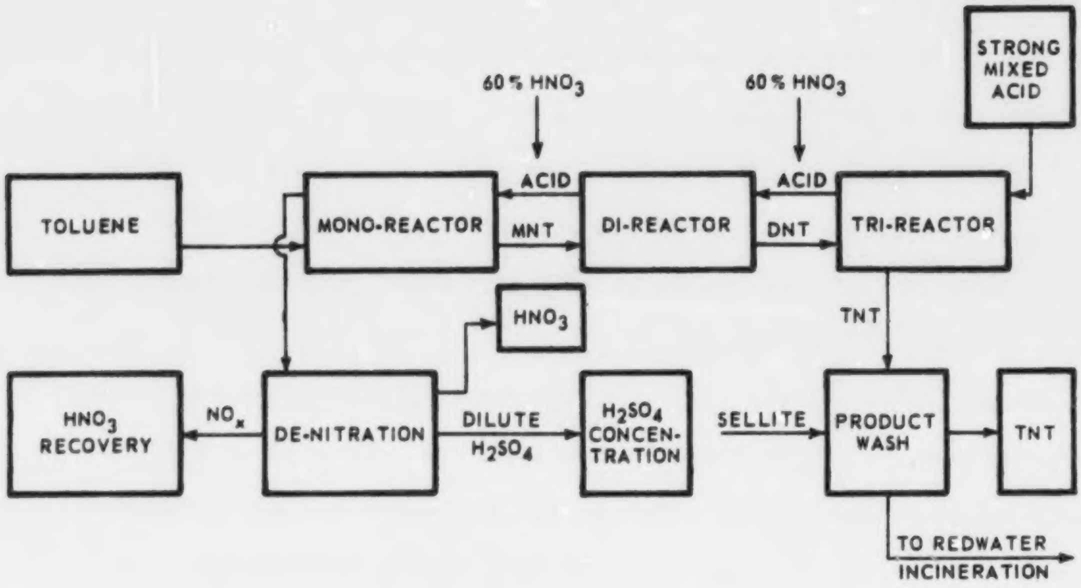

STRONG MIXED ACID
60% HNO3
60% HNO3
TOLUENE
MONO-REACTOR
ACID
MNT
DI-REACTOR
ACID
DNT
TRI-REACTOR
HNO3
TNT
HNO3 RECOVERY
NOx
DE-NITRATION
DILUTE H2SO4
H2SO4 CONCEN-TRATION
SELLITE
PRODUCT WASH
TNT
TO REDWATER INCINERATION

Figure 3-14. Trinitrotoluene (TNT) manufacturing diagram.

denitrator noncondensibles in an absorption tower for nitric acid recovery to minimize net acid consumption.

NO_x emissions from nitration reactors at the new Ordnance Works at Newport, Indiana, have been estimated at 1.24 kg/1 000 kg of TNT. The NO_x concentration was estimated at 400 ppm.[48] Another ammunition plant, where the equipment was old and overloaded, generated about 59 000 kg/day.[49,50] Assuming that the average TNT plant emits twice as much NO_x as the new plant and that no NO_x is emitted in NG manufacture,[45] emissions from commercial explosives (Table 3-15) are roughly estimated as reported in Table 3-16. The estimated emission by producing explosives in the BRD (1970) are about 0.9 Mkg NO_2.*

Redwater is made only in the manufacture of military TNT.[45] Washing out isomers and other impurities that make TNT sensitive to shock is necessary, since military ammunition must be insensitive to handling.

Other sources of NO_x at the Newport plant were denitration of spent mixed acid, nitric acid concentration, and nitric acid production. The first two emitted about 6 kg/1 000 kg of nitric acid after 75-percent reduction in a fume burner; the concentration of these emissions was estimated at 1.7 percent, probably all NO.

Oxygen balance is the most important factor affecting the NO_x content of the products of explosions. An oxygen-balanced explosive contains just enough oxygen to oxidize all carbon to carbon dioxide and all hydrogen to water. A deficiency of oxygen produces toxic carbon monoxide; an excess produces NO_x.[43,44] Because AN contains one excess atom of oxygen per molecule, combustible materials (e.g., 5 percent fuel oil), are usually added to AN to provide oxygen balance and to increase power. NG has a slight oxygen surplus; TNT has a shortage.

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*For the used emissions factors see: "Compilation of Air Pollutant Emissions Factors". U.S. Dept. of Health, Education, and Welfare 1972.

Table 3-16. TOTAL UNITED STATES NITRIC ACID REQUIREMENTS AND NO_x EMISSIONS FROM MANUFACTURE OF INDUSTRIAL EXPLOSIVES, 1967

Explosion product and emission source	TNT production, 1 000 kg	HNO_3 used 1 000 kg	NO_x, kg/1 000 kg HNO_3	NO_x, 1 000 kg/yr	NO_x, kg/kg product
TNT (industrial use)	9 000	9 000	—	—	—
Reactor emissions	--	--	2.5	23.0	0.003

Table 3-17. NO_x IN PRODUCTS OF EXPLOSIONS

Explosive	NO_x, %	NO_x, kg/1 000/kg explosive
TNT, 50-50 Amatol, RDX, tetryl, straight dynamites, AN-fuel-oil mixture	0	0
AN/DNT	0	0
PETN	0.3-0.6	5-9
Nitroglycerin	1.5	23
Straight gelatins, 40%	0.1	1.5
Straight gelatins, 75%	0.1	1.5

Information on compositions of the products of explosions is usually obtained by computer calculations.[43] Calculated NO_x in products from various explosives are listed in Table 3-17.

The NO_x generated in commercial explosions in 1967 was probably less than 90 720 kg since most of the 25.4 Mkg of NG was used in oxygen-balanced explosives.[45] Explosions could be an intense, but small, source in confined underground spaces.

3.3.2.5 Other Nitric Acid Uses--Nitric acid is used for acidulation of phosphate rock and limestone in fertilizers, for the treating of metals, and for rocket fuel oxidation.

Fertilizers--In the United States, sulfuric and phosphoric acids are used in acidulating phosphate rock. A few manufacturers first acidulate with nitric acid to form phosphoric acid and calcium nitrate and then add ammonia with either carbon dioxide, sulfuric acid, or phosphoric acid. Dibasic calcium phosphate and ammonium nitrate are the useful compounds produced.[51] Private sources indicate that nitric phosphate fertilizers made by acidulation of phosphoric rock totaled 454 Mkg and consumed 136 Mkg of nitric acid in 1967.

NO_x is formed as nitric acid oxidizes the carbonaceous matter in the rock. Although no measurements of NO_x emissions are available, brown plumes have been observed. The use of water scrubbing by fertilizer manufacturers to reduce the major emissions of particulates and fluoride probably reduces NO_x only slightly. The addition of urea to the acidulation mixture reduces NO_x emissions and eliminates the brown plume.[52] The use of calcined rock also avoids the formation of NO_x.

Metals pickling--The principal use of nitric acid in metals pickling is removing mill scales from stainless steels. Pickling procedures vary.

One procedure uses a 10 percent sulfuric acid bath at 330 to 340 K followed by a bath at 320 to 330 K with 10 percent nitric acid and 4 percent hydrofluoric acid; the first bath loosens the scale, and the second removes it. Another procedure is a continuous system of two tanks containing 15 percent hydrochloric acid followed by a tank containing 4 percent hydrofluoric and 10 percent nitric acid at 330 to 340 K. Still another effective method is to follow an agent such as sodium hydride mixed with molten salts of sodium hydroxide with a dilute nitric acid wash.[53] For treating stainless steel, nitric acid is preferred to other acids because it does not attack the metal itself.

Nitric acid is also used for bright-dipping copper and for the chemical milling of copper or iron from metals that are not attacked by the acid. The former operation usually requires a cold solution of nitric and sulfuric acids, but cold nitric acid with urea added is also effective. (Adding sulfuric acid to the nitric acid-urea mixture forms nitrourea, an explosive, and is not recommended.) Addition of 45 to 60 kg/m^3 of 40 percent nitric acid reduces NO_2 emissions from 8 000 to less than 10 ppm, if a bubble disperser is used,[54] and gives an acceptable finish without formation of NO_x fumes.

A small but intense source of NO_x is the manufacture of tungsten filaments for lightbulbs. Filaments are wound on molybdenum cores, which are heated and dissolved in nitric acid. Decker[55] has commented on a technique for reducing NO_2 fumes given off periodically when trays of filaments are dissolved: a charcoal bed adsorbs NO_x as fumes are generated and desorbs when no fumes are being generated, and thus limits the variations in NO_x content in offgases; combining the gases with carbon monoxide and hydrogen from a rich combustion flame and passing the mixture through a bed of noble metal catalyst releases a colorless gas.

3.3.3 Petroleum and Natural Gas Industries

Three industrial sources--oil and gas production, gas plants, and pipeline stations--are usually in remote areas; the fourth source, petroleum refineries, is often in or near densely populated areas. Mobile sources are not discussed in this report. Oil and gas production includes drilling, oilwell pumping, gathering, gas-water injection to the producing formation, and oil dehydration. Gas plant operations include removal of impurities (e.g., water and surface compounds) and recovery of natural gas liquids (e.g., ethane, propane, butane, and natural gasoline.) Pipeline stations deliver the energy to move product from its source to its demand point.

Of these operations, petroleum refining is by far the most involved. Petroleum refining converts crude oil into salable products (Fig. 3-15). In an atmospheric pipestill, light products are separated from crude and taken overhead; light catalytic reforming feed, raw gasoline, kerosene, middle distillate, and heavy gas-oil are taken as sidestream products. The reduced crude, used in making asphalt and residual fuels, is charged to a vacuum pipestill where heavy gas-oil, lube stocks, and residuum are cut or is fed to coking to increase the yield of distillate products. Atmospheric and vacuum gas-oils charge to catalytic cracking units produce light ends, cracked gasoline, and fractions for blending distillate and residual fuels. Subsequent operations include catalytic cracking and coking, catalytic reforming, or hydrogen treating.

Catalytic cracking and coking produce propylene and butylene, which are often treated with isobutane to make alkylates or polymerized for use in gasoline or chemical production. Catalytic reforming increases the octane number of naphtha by converting naphthenes (saturated cyclin hydrocarbons) and paraffins to aromatics. Hydrogen treating decreases sulfur

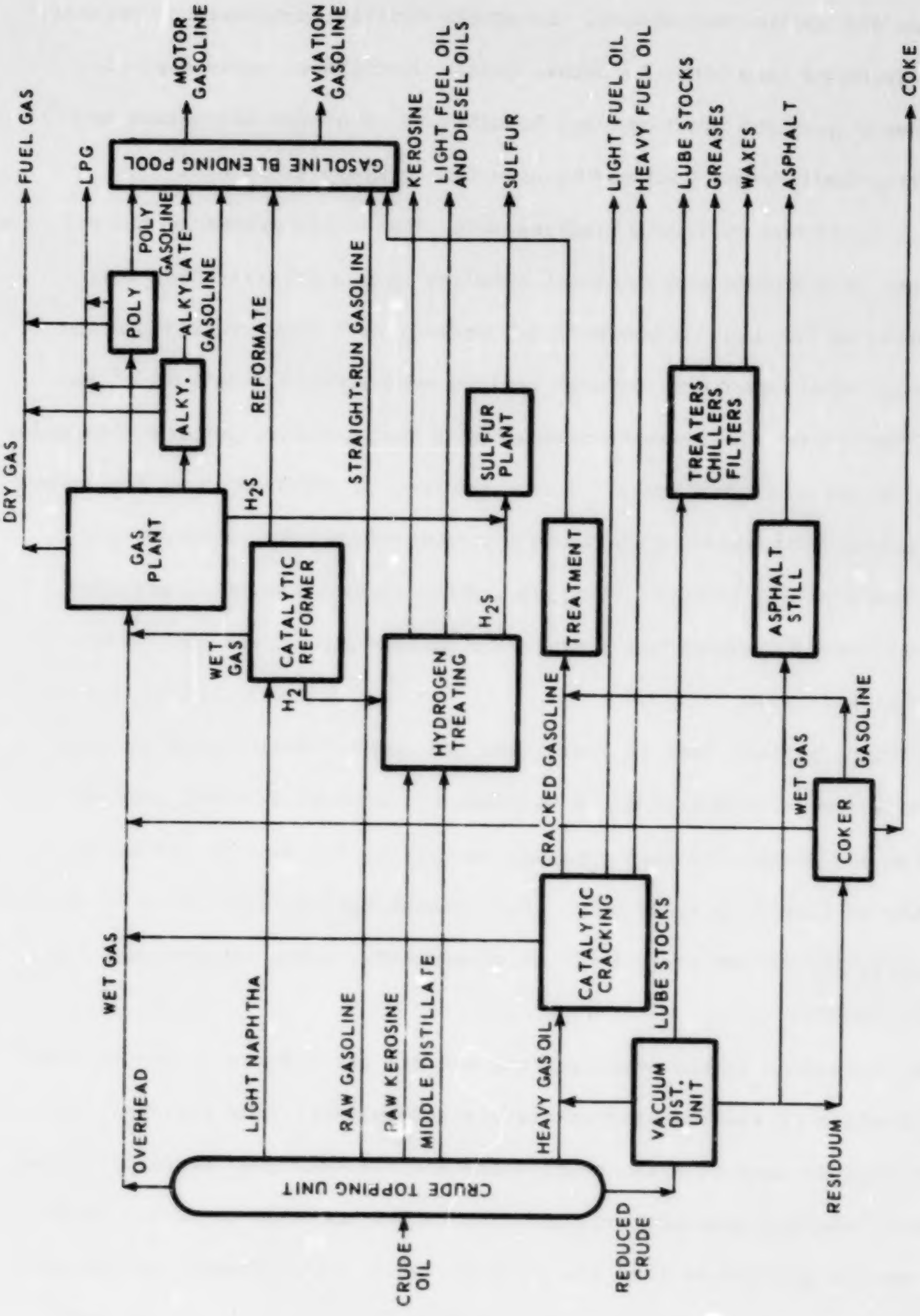
CRUDE OIL
CRUDE TOPPING UNIT
REDUCED CRUDE
OVERHEAD
LIGHT NAPHTHA
RAW GASOLINE
RAW KEROSINE
MIDDLE DISTILLATE
HEAVY GAS OIL
VACUUM DIST. UNIT
RESIDUUM
LUBE STOCKS
WET GAS
CATALYTIC CRACKING
CRACKED GASOLINE
COKER
WET GAS
GASOLINE
ASPHALT STILL
TREATMENT
TREATERS CHILLERS FILTERS
HYDROGEN TREATING
H_2
WET GAS
CATALYTIC REFORMER
H_2S
GAS PLANT
DRY GAS
H_2S
SULFUR PLANT
STRAIGHT-RUN GASOLINE
REFORMATE
ALKY.
POLY
ALKYLATE GASOLINE
POLY GASOLINE
GASOLINE BLENDING POOL
FUEL GAS
LPG
MOTOR GASOLINE
AVIATION GASOLINE
KEROSINE
LIGHT FUEL OIL AND DIESEL OILS
SULFUR
LIGHT FUEL OIL
HEAVY FUEL OIL
LUBE STOCKS
GREASES
WAXES
ASPHALT
COKE

Figure 3-15. Composite processing plan for a modern refinery.

content, increases stability, and improves burning characteristics of kerosenes and middle distillates. To attain desired quantities of refined, salable products (gasoline, kerosens, middle distillate, heavy fuel oil, etc.), heavy gasoline fractions may be diverted to middle distillate and catcracking feed, coker feed may be diverted to heavy fuel, etc.

In a fluid-bed catalytic cracking unit (Fig. 3-16) preheated gas-oil is charged to a moving stream of hot catalyst during transfer from the regenerator to the reactor where it is cracked; both the products and the regenerator flue gases pass through cyclone separators for removal of entrained catalyst. The products then go to a fractionator, and the flue gases are discharged through a stack. Spent catalyst is withdrawn from the bottom of the reactor, transferred to the regenerator where coke is burned off, and returned to the reactor. Flue gas, which contains about 10 percent carbon monoxide, is sometimes burned with auxiliary fuel and preheated air to generate steam.

Refinery process heaters are either the cabin furnace, used for heat releases above 84.4 GJ/hr or the vertical cylindrical furnace, used for less than 158 GJ/hr. (Either type may be used in the 84.4 to 158 GJ/hr. Fuels may be liquid, gas, or both. Gas burners operate with 10 to 40 percent excess air, liquid burners with 20 to 80 percent. Stack temperatures are 470 K to 750 K.

NO_x emissions in the petroleum and natural gas industries result from the combustion of fuel in process heaters and boilers, from internal combustion engines used to drive compressors and electric generators, from the catalytic-cracking regenerators, and from carbon monoxide burners. Estimated amounts emitted in 1967 are shown in Table 3-18. Diesel oil consumption was estimated as residual plus diesel fuel oil in "oil-company use"[60]

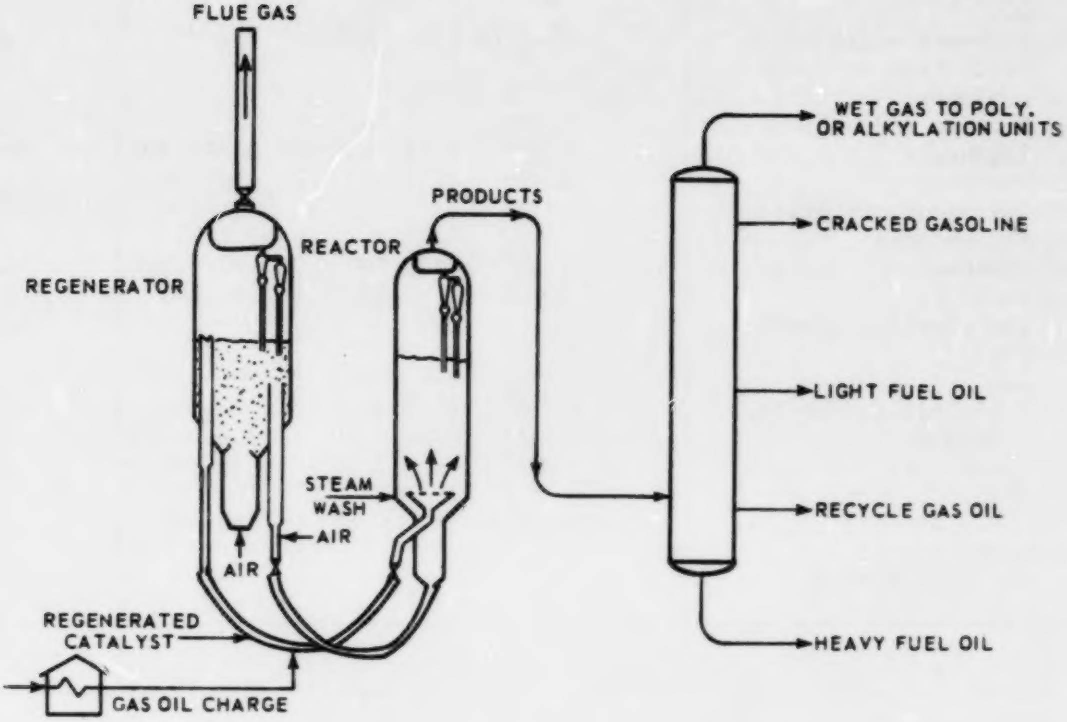
FLUE GAS
REGENERATOR
REACTOR
PRODUCTS
WET GAS TO POLY. OR ALKYLATION UNITS
CRACKED GASOLINE
LIGHT FUEL OIL
RECYCLE GAS OIL
HEAVY FUEL OIL
STEAM WASH
AIR
AIR
REGENERATED CATALYST
GAS OIL CHARGE

Figure 3-16. Fluidized-bed catalytic cracking unit (FCC).

Table 3-18. NO_x EMISSIONS FROM PETROLEUM AND NATURAL GAS OPERATIONS IN THE UNITED STATES, 1967

Operations	Fuel consumption[a]	Emission factor[b]	NO_x emissions	
			Range, ppm	Quantity, Mkg/yr
Oil and gas production				
Gas				
Heaters and boilers	14.00[c]	3 200[d]	25-200	45
Engines	3.50[c]	12 300[e]	250-2 500	44
Oil				
Diesel engines	1170[f,g]	26[h]		31
Production subtotal				120
Gas plants				
Heaters and boilers	7.00[c]	3 040[d]	25-200	12
Engines	7.35[c]	68 800[e]	1 000-3 500	509
Turbines	0.42[c]	3 200[i]	50-200	2
Gas plant subtotal				523
Gas pipelines				
Engines	12.33[c]	116 900[e]	1 500-3 500	1 448
Turbines	3.96[c]	3 200[i]	50-200	13
Gas pipeline subtotal				1 461
Refining				
Gas				
Heaters and boilers	46.90[f]	3 360[d]	25-200	157
Engines	1.32[f]	69 630[e]	1 000-3 500	79
Turgines	1.52[f]	3 200[i]	50-200	5
Oil				
Heaters and boilers	6400[f]	8[h]	50-400	51
Other				8
Refining subtotal				300
Total NO_x emissions				2 404

[a] Oil consumption as dm^3/yr.
Gas consumption as km^3/yr.

[b] Oil emission factors--kg/m^3.
Gas emission factors—μkg/m^3.

[c] Reference 56.

[d] Reference 57.

[e] Reference 58.

[f] Reference 59.

[g] Reference 60.

[h] Reference 61.

[i] See Table 3-5.

minus fuel oil "consumed at refineries;"[59] all diesel oil was assumed to have been used in diesel engine prime movers—the use with the highest emission factor. Gas consumption in oil and gas production was estimated by subtracting gas used in gas plants and estimated losses from the gas field-use;[56] gas consumption for refineries (i.e., natural gas, LPG, and refinery gas) was calculated as natural gas, on the basis of combustion heat; oil consumption includes acid sludge.[59] For gas plants and for refineries, consumption by "heaters and boilers," "engines," and "turbines" was based on capacities indicated by Pipe Line Industry.[57,62,63]

Emission factors for gas-fired heaters are derived from Fig. 3-17. This relationship between NO_x production rate and fuel-firing rate and the sizes of furnaces and engines for various applications is based on the survey of the petroleum and natural gas industries.[57,62] Emission factors for diesel engines and oil-fired furnaces are from Duprey. Emission factors for gas engines are based on Fig. 3-18, which is reproduced from the studies of Mills et al,[64] and emission factors for gas-turbine engines are from Table 3-18.

Estimated NO_x emissions from catalytic-cracking regenerators are 2.7 Mkg/yr and from carbon monoxide boilers are 5.5 Mkg/hr. Cracking 670 000 m^3/day of fresh feed[65] emits NO_x at a rate of 0.011 kg/m^3.[64] The 0.11 kg/m^3 is a weighted average for fluid and moving-bed catalytic-cracking units; NO_x in catalytic-cracker flue gas would be about 10 times as much, based on Duprey's factors,[38] which are not consistent with other data.[64] In the BRD there is a catalytic cracker capacity of about 6.6 Gkg of crude oil. With an emission factor of 0.17 kg/m^3 fresh feed*, there results an NO_2 emission of about 1.53 Mkg of NO_2.

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*For the used emissions factors see: "Compilation of Air Pollutant Emissions Factors". U.S. Dept. of Health, Education, and Welfare 1972.

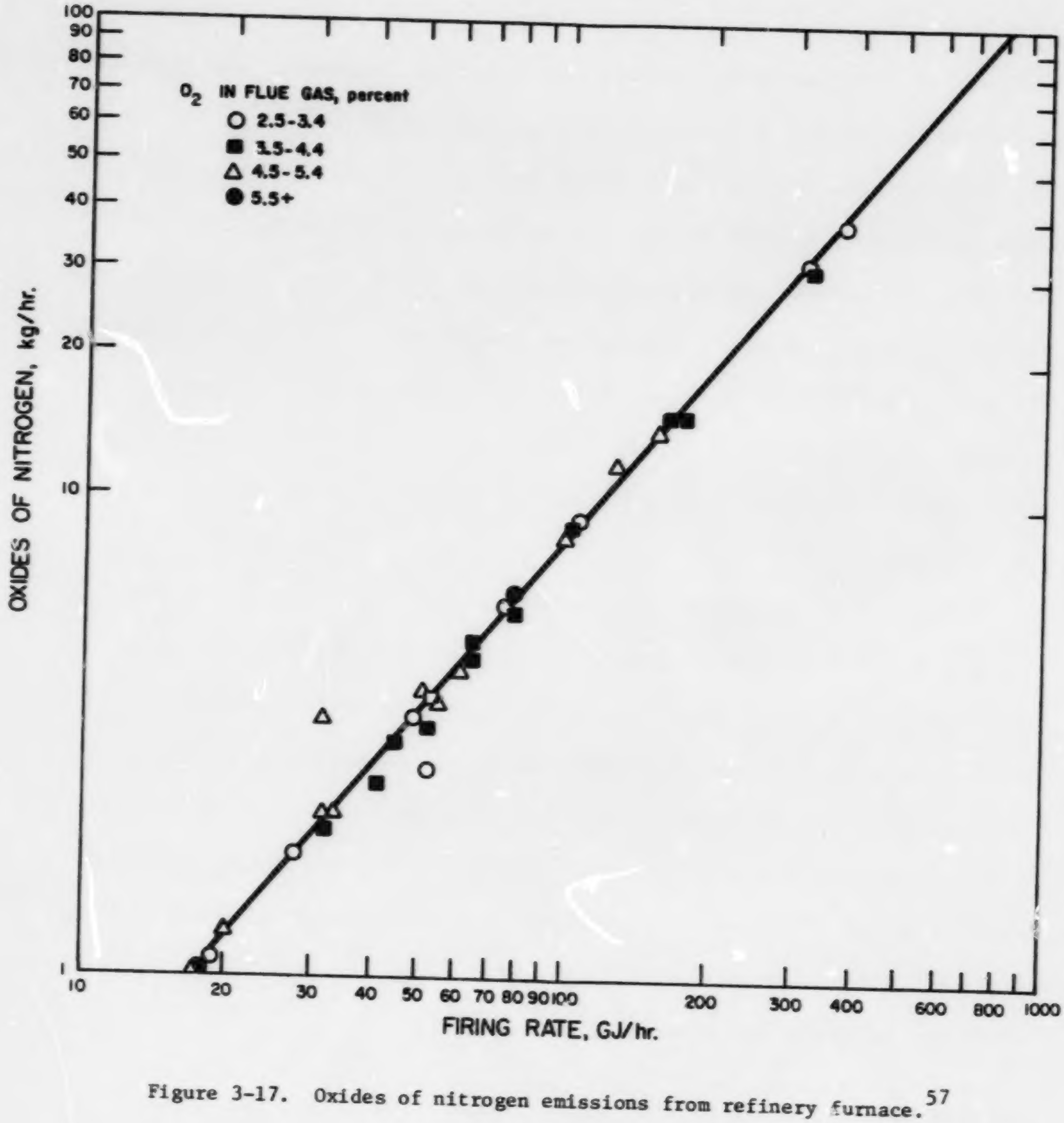

Figure 3-17. Oxides of nitrogen emissions from refinery furnace.[57]

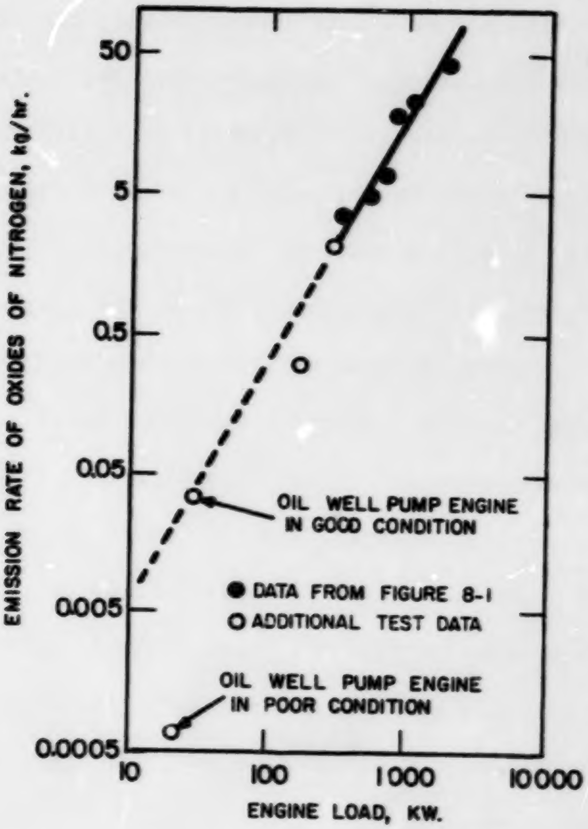

Figure 3-18. Variation is oxides of nitrogen emission rates from stationary internal combustion engines.[58]

Each of 75 carbon monoxide boilers in the United States[66] emits an estimated 9.5 kg/hr. Data reported by Mills et al.[64] would give 40.8 Mkg/hr of NO_x; this is greater than the amount generated in a conventional furnace with much higher flame temperatures, and thus thought to be too high.

Few data are available for gas engines, and the emission factors may not be representative. In Fig. 3-18, the high values for large gas engines probably reflect lean combustion mixtures, supercharging, low speed, and other variables that favor high NO_x emissions (Section 5.3); the values for smaller engines are probably for naturally aspirated engines, operated at higher speeds with rich combustion mixtures--variables that favor low NO_x. The plotted values reported by Mills et al.[67] probably reflect these variables, not size per se. Thus, Fig. 3-18 is a means of interpolation. Extrapolation of the correlation for engines larger than 1490 kW, the largest size tested, was not done; emission factors derived for the 1490 kW engine were applied to larger engines. Duprey's emission factor, based on tests of gas engines averaging about 261 kW [58] results in estimated pipeline and gas plant emissions of only 181 and 127 Mkg/yr of NO_x.

NO_x sources in the petroleum and natural gas industries as percentages of the total from all U.S. sources in 1967 are given in Table 3-19. The inhouse use of the refineries in the BRD is estimated for fuel oil as 4.2 Gkg and for refinery gas about 7×10^8 m^3 (138×10^{15}J), this generates about 53.5 Mkg NO_x (estimated as NO_2).

3.3.4. Metallurgical Process

Emissions from metallurgical processes occur in conjuncion with pig iron production and steel production.

3.3.4.1 Pig Iron Production--The blast furnace is the central unit for reducing iron ore in the presence of coke and limestone to produce pig

Table 3-19. NITROGEN OXIDE EMISSIONS FROM PETROLEUM AND NATURAL GAS OPERATIONS IN UNITED STATES, 1967

Operations	Percent of total 1967 emissions
Oil and gas production	0.8
Gas plant	3.7
Pipeline	10.3
Refining	2.1
Total	16.9

iron. The only pertinent reaction occurs when the hot air blast, supplied to the furnace from a blast furnace stove through nozzle-like openings called tuyeres, contacts the coke and releases carbon monoxide. Excess carbon monoxide (beyond that needed in reducing the ore), plus the other gases and particulates, makes up the 3 630 to 4 540 kg of blast furnace gas generated per ton of pig iron produced. This gas contains about 1 percent hydrogen and 27 percent carbon monoxide; it has a heating value of approximately 3 430 kJ/m^3.[68] Some 18 to 24 percent of this gas is used as fuel to heat the three stoves (two on heat, one on blast) usually associated with each blast furnace.

A blast furnace stove (some 7.9 to 8.5 m in diameter and 36.6 m high) has a roughly cylindrical combustion chamber extending to the top and checkerwork heating surface at the bottom. Combustion gases pass through this brick checkerwork by reverse flow and then to the stack. Unlike conventional regenerators (which extract heat from waste combustion gases), the stove burns fuel and stores heat which is subsequently used to preheat air for the furnace.

The low caloric value of blast furnace gas indicates that, due to dilution and to low flame temperature, the NO_x content of the off-gas from the stove is low (from 1.7 to 6.6 ppm NO_x, averaging 3.6 ppm). However, the NO_x emission is estimated at 11.8 kg/hr or 103 000 kg/yr for a typical blast furnace. January 1, 1969, 154 furnaces were on blast in the United States;[69] these would release 15.7 Mkg/hr, or 0.6 percent of the estimated 1965 total U.S. industrial NO_x emissions.[70]

In 1971 there were 71 blast furnaces working in the BRD (about 70% of the 98 installed ones). With an estimated NO_x-emission factor of 11.7 kg/hr or 114 000 kg/yr for a typical blast furnace, there will be in the BRD about 10.71 Mkg NO_x emissions (estimated as NO_2).

3.3.4.2 Steel Production--Steelmaking in the United States by the open hearth process has been decreasing since its peak in 1956; it then represented 90 percent, or 93.5 Gkg, of the total production. In 1967, production declined to 55 percent. By 1972, it may be only 22.7 Gkg. Phaseout of this process is expected between 1980 and 1990.[71] Steel production in the BRD 1950-1971 is given in Figure 3-19.

Open hearth furnace--This type furnace, like glass-melting furnaces (Section 3.3.6), is both reverberatory and regenerative. It is reverberatory because the charge is melted in a shallow hearth by a flame passing over the charge and by radiation from the heated dome. It is regenerative because heat from the combustion gases from the reverberatory chamber accumulates in a brick-filled chamber, or "checker," and preheats the incoming air when the cycle reverses. Fuel (e.g., blast furnace gas) as well as combustion air are preheated by the checkers to obtain the high temperatures required.

In an open hearth furnace, the charge (hot metal from the blast furnace plus pig iron, scrape iron, and lime) is heated about 10 hours with fuel oil (the preferred fuel) and excess air at a temperature as high as the refractory permits. These conditions favor NO_x formation. An analysis of 10 open hearth stack samples shows an emission range of 22.9 to 671 ppm, at an average of 243 ppm. A series of tests averaged 320 ppm. These analyses were taken while an oxygen lance was in use to enhance the steel-producing reactions.[73]

It is estimated that 220 kg of NO_x are emitted in the production of a 181 000 kg batch of steel. These calculations are based on the use of 3.7 MJ/kg of steel[74] and production of 0.32 nKg/J of NO_x. In 1969, the U.S. production of steel was 128 000 Mkg,[69] 43 percent of which was produced

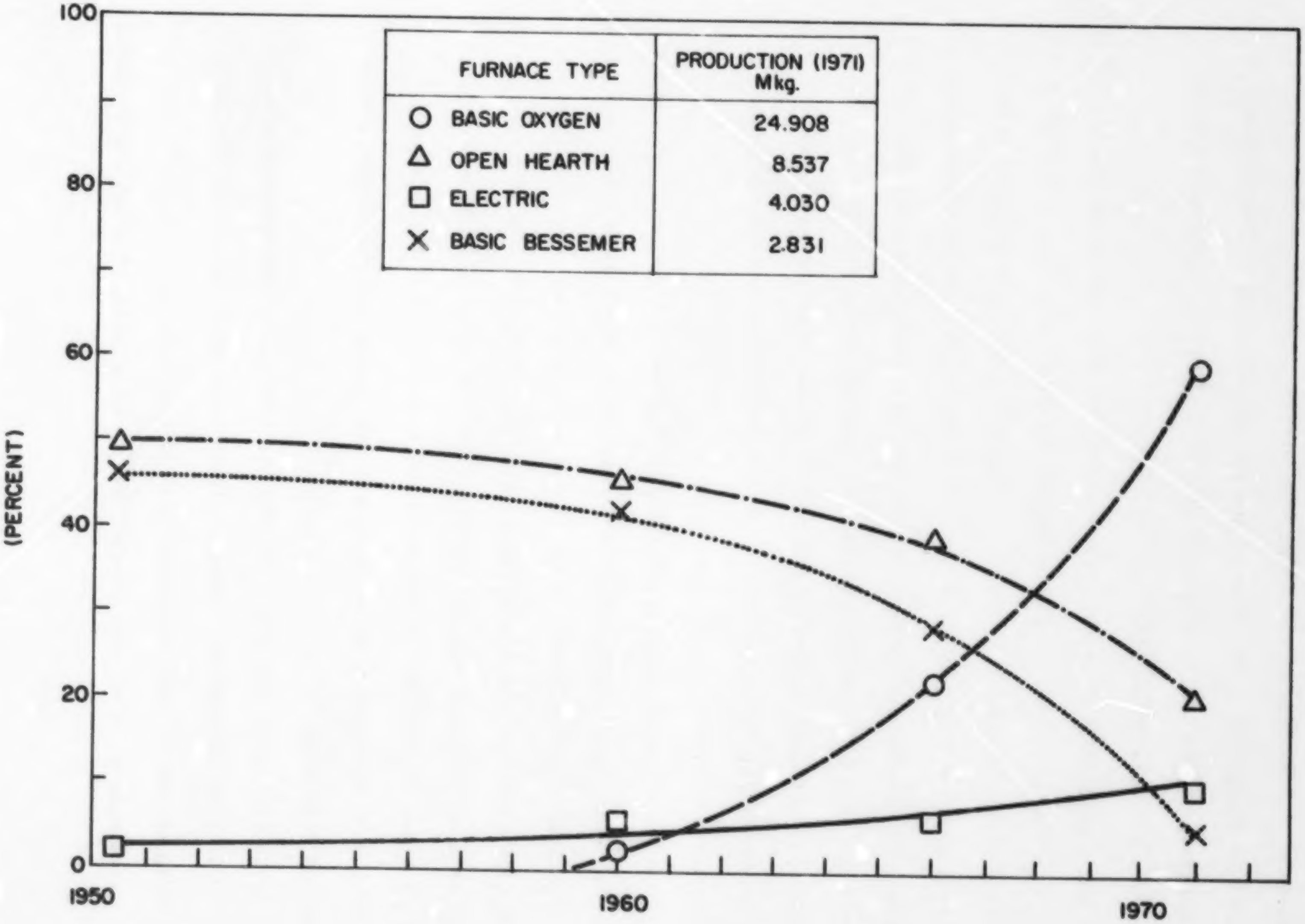

Figure 3-19 Steel production in the Brd, 1950-1971.[72]

in open hearth furnaces. This accounts for roughly 67.1 Mkg of NO_x emissions, which is 2.7 percent of the estimated 1965 industrial NO_x emissions in the United States.[71] With an estimated emission rate of 339 kg NO_2 per 200 000 kg batch of steel in the BRD, there are about 15.3 Mkg NO_x (estimated as NO_2) released in 1971.

Coking ovens-- Coke is essential in making pig iron and steel, and coke ovens are generally an integral part of the steel plant complex. Conventional coking is done in long rows of slot-type ovens with sidewalls or liners of silica brick and spaces or flues between the chambers where fuel burns to supply heat. Each kilogram of coal charged through holes in the top of the ovens and carbonized requires 2.3 to 2.7 MJ and flue temperatures as high as 1 750 K.[75] The 18-hour heating period for destructive distillation of the coal produces noncondensable coke oven gas, which on a dry basis has a heating value of about 21 200 kJ/m^3. Approximately 35 percent of this gas is used in heating the oven. Heat from the combustion gases accumulates in a brick checkerwork and preheats the combustion air when the cycle reverses; this regenerative cycle conserves fuel and increases flame temperatures.

In 1969, the United States produced 58 Gkg of coke from 84.5 Gkg of bituminous coal. On the average, coal requirements were 1.46 kg/kg of coke produced.[69]

The trend in new construction is higher coke ovens--5.0 to 5.8 m instead of the usual 4.0 to 4.3 m--to increase coal throughput by 75 percent.[76] This increase, due in part to higher temperatures permitted by improved refractories and more uniform heating designs, will increase NO_x emissions.

Analysis of two coke oven stack gas samples gave values of 41 to 50 ppm NO_x, an average of 45 ppm. Another test averaged 28 ppm.[73] In 1967, the carbonization of 83.5 Gkg of coal emitted more than 5.5 Mkg of NO_x, or 0.23 percent of the 1965 United States industrial NO_x emissions.[71] According to American emission patterns there were about 765 000 kg NO_x (estimated as NO_2) emitted from coke production in the BRD (1971).

Cupola furnaces--The cupola furnace is similar to the blast furnace. Its function is to melt scrap and pig iron for subsequent processing in steel production. Its offgas contains recoverable carbon monoxide which can be burned to preheat the air blast.[76]

Reducing conditions in the cupola furnace do not produce the quantity of NO_x that the high temperatures suggest. Data indicate 13 ppm NO_x in the vent gases, or 0.05 kg/1 000 kg of metal produced.[64] A questionnaire survey of 1 680 United States foundries shows that 13.2 Gkg of iron-casting shipments were produced by cupolas in 1966; on this basis, iron cupolas emitted 730 000 kg of NO_x. The production of iron castings in the BRD is about 4.3 Gkg yearly (1960-1971).[77] The NO_x emission, compared to other emissions, is negligible (306×10^3 kg NO_2/year).

Basic oxygen furnaces--Bottom-flowing, characteristic of the Bessemer refining process for steel production since 1870, has been rapidly replaced by top-blowing--now a major refining process. Top-blowing, using commercially pure oxygen, is characteristic of the basic oxygen furnace (BOF).[78]

If the carbon monoxide is permitted to burn off, NO_x is formed when hot gas reacts with air outside the furnace (30 to 80 ppm, or 0.18 to 0.5 kg/1 000 kg of steel).[79] This can be avoided by use of a suitable hood system to collect the gas for other purposes, but if these other purposes include use as fuel, some NO_x may still be produced.

Other furnaces--Furnaces using either regenerative or recuperative preheat of the combustion air are also used as reheating and soaking pit furnaces. Analysis of soaking pit stack gases has given average NO_x values of 25.8 and 21.5 ppm.[73] These values are consistent with coke oven emissions (45.6 and 28.3 ppm) but considerably lower than open hearth values (243 and 320 ppm). NO_x emissions from soaking pit stack gases are estimated at 4.99 Mkg/yr in the United States, based on 0.04 kg/1 000 kg of ingot steel produced and a total production of 115 Gkg/yr.[64,73]

Sintering operations--Sintering operations differ somewhat from conventional furnace operations. Fine iron-bearing material is mixed with a fuel (e.g., coke breeze), spread on a traveling grate, and ignited by gas burners; combustion, maintained by air drawn down through the grate, yields a product for blast furnace use. Analysis of stack gases from sintering produces NO_x values of 47.2 to 36.3 ppm.[73] NO_x from sintering stack gases are estimated at 24.5 Mkg in the United States, based on 0.5 kg/1 000 kg of sinter[73] and sinter production of 46.3 Gkg/yr.[64] NO_x from sintering stack gases are estimated at about 24.5 Mkg/hr (calculated as NO_2), based on 0.72 kg/1 000 kg of sinter production of about 32 Gkg/yr.[77,80]

Emissions in the steel industry and its related processing are mainly fumes, smoke, and dust or particulates. Usually considered obnoxious are sulfur dioxide, carbon monoxide, and odors. Physical evidence of NO_x has been obscured by the heavy emission of particulates. The NO_x emissions which occur have been traced largely to the combustion of fuel oils and gas and, in part, to the burning of carbon monoxide, a product of the processing.

3.3.5 Kilns--Cement, Limestone, and Ceramics

The kiln--rotary, vertical, tunnel, or beehive--is used in the production of cement clinker and quicklime and in the firing of ceramic products.

The rotary kiln predominates the cement industry. Both the rotary and the vertical shaft kiln are used extensively for limestone calcining. For ceramic firing, the tunnel kiln is used for the smaller, more fragile items and the beehive kiln for larger items such as drainage pipe.

Cement clinker is produced by gradually heating intimately ground mixtures of limestone with suitable clays, shales, or marls (either as dry feed or wet slurry) up to 1 870 K[81] in rotary kilns. A rotary kiln is a steel cylinder, 2.5 to 7.6 m wide and 45.7 to 213.5 m long, lined with a refractory material, slightly inclined, and rotated at about 1 rpm. Raw feed entering at the high end is partially melted in the nonreducing atmosphere as it tumbles to the lower end over a period of 2 to 4 hours; combustion gases rise from the lower end where the fuel is fired with excess preheated air. Incoming combustion air is heated by the clinker, which improves the overall thermal efficiency and gives a higher peak temperature. The clinker, when finely ground and mixed with a small amount of gypsum to control set, is commercial portland cement.

The capacity of individual kilns has been increased in recent years to more than 17 Mkg/day, but 3.4 to 7.7 Mkg/day is representative of the industry. In 1967, 183 United States plants produced about 67 Gkg of cement [69] and used an average of 7.74 GJ/1 000 kg of cement (Table 3-20). In the BRD the fuel consumed by cement industry is given in Table 3-21; the BRD produces 35 Gkg of cement annually in 96 plants.[82,83]

Vertical kilns, first used for limestone calcination, have been largely replaced with rotary kilns, but a few new and improved vertical kilns have been announced.[84] The capacity limit, which was a major disadvantage, has been increased to 454 000 kg/day, the equivalent of modern rotary kilns.

Table 3-20. FUEL CONSUMED BY U.S. CEMENT INDUSTRY, 1967

Fuel	Amount consumed	Equivalent heating value, TJ	Percent of total
Coal	8 252 Mkg	249 000	51
Oil	793 dam^3	32 000	7
Natural gas	4 500 hm^3	207 000	42

Table 3-21. FUEL CONSUMED BY THE BRD CEMENT INDUSTRY, 1971

Fuel	Amount consumed	Equivalent heating value, TJ	Percent of total
Coal	300 Mkg	9 400	5
Fuel oil			
Distillate	22 Mkg	900	68
Residual	2 800 Mkg	117 200	
Natural gas	935 hm^3	32 700	19
Sewer gas	6.6 hm^3		
Current	3.8×10^9 kWh	13 700	8
Total		173 900	100

Table 3-22. FUEL CONSUMED BY THE BRD LIME INDUSTRY, 1971

Fuel	Amount consumed	Equivalent heating value, TJ	Percent
Coal	810 Mkg	25 500	50
Oil			
Distillate	74 Mkg	3 100	6
Residual	109 Mkg	4 600	9
Natural gas	468×10^6 m^3	16 300	31
Sewer gas	3×10^6 m^3		
Electricity	576×10^6 kWh	2 100	4
Total		51 600	100

Vertical kilns are more efficient thermally than rotary kilns: 5.81 MJ/kg[84] for vertical and 8.14 MJ/kg for rotary.

If limestone rock is almost entirely calcium carbonate ($CaCO_3$), it is known as a high calcium limestone. If 30 to 45 percent of the calcium carbonate is displaced by magnesium carbonate ($MgCO_3$), it is known as a dolomitic limestone. Either of these limestones, when heated, loses carbon dioxide (CO_2) and forms quicklime; excess heat must be avoided if a high quality or active quicklime is desired; long heating at sintering temperature 1199 to 1615 K produces dead-burned dolomitic lime for refractory furnace linings. Product heat is recovered to preheat the combustion air. The heat dissociates the limestone by proceeding inward from the outer surface of the stone particle as higher temperatures are induced. Since a gradual temperature increases is preferred, the rotary kiln is particularly suited to limestone calcination.

The 1968 U.S. production of lime was 16.80 Gkg in 206 plants. Of this total, 63 percent was produced in 33 plants.[69] A value of 7 MJ/kg was used to estimate the 1968 thermal requirements at 118 000 TJ. Lime industry production in the BRD in 1971 is given in Table 3-22.

The ceramics industry produces a multitude of products including refractories, vitreous enamels, withewares, abrasives, structural clay products, and ceramic minerals. The larger kilns are of two types: tunnel and beehive. The tunnel kiln is 0.61 to 3.05 m wide, 1.22 to 2.44 m high, and 22.8 to 30.5 m long, with gas-or oil-fired burners placed near its center. The material being fired moves slowly into the hot zone and cools slowly in the remaining length of travel; the combustion air enters at the exit end and is preheated as it contacts the hotware in the kiln. In beehive-shaped kilns up to 18.3 m in diameter, the burners are spaced around the periphery; combustion gases are diverted toward the dome, down through the ceramic material stacked on the floor, and into ducts under the floor that lead to a stack, which usually serves four kilns.

Particulates are the pollutants primarily associated with cement, lime, and ceramic kilns, but significant NO_x formation is anticipated in cement and lime kilns. Accordingly, estimated NO_x emissions in the United States during 1967 appear in Table 3-23, based on fuel consumption (Section 3) and on correlations between the rate of NO_x production and the heat input to the combustion unit[85] (Fig. 3-20). Estimated NO_2 emissions from kilns in the BRD are given in Table 3-24. Limited data have been reported on NO_x emissions from tunnel and beehive ceramic kilns. For gas-fired tunnel kilns used for items such as pottery, the results of five tests varied from 3 to 66 ppm, with an average of 24 ppm.[87] A beehive kiln which can accommodate 907 000 kg of ceramic ware requires a heat input of up to 15.8 GJ/hr. Based on estimated emission factors, it will produce 1 kg/hr of NO_x if gas fired and 2.2 if oil fired; if four kilns are served by a single stack, the NO_x emissions will be 4 kg/hr for gas and 8.6 kg/hr for oil.

3.3.6 Glass Manufacture

The glass-manufacturing industry produces glass containers, fiber-glass, flat glass, and specialty glass. Raw materials are primarily silica sand, soda ash, limestone, and cullet (crushed waste glass). To melt these materials into a viscous liquid, for the production of window and plate glass, for example, 1 780 to 1 840 K may be required. Gas is the most often used of all, fuel oil is second choice, and coal is not used in glass melting. Since molten glass is conductive, electric heating is used to supplement fuel firing whenever technically and economically practical. To melt a few thousand kilograms of specialty glass, pot-type furnaces are used; the continuous tank type is used for larger quantitites.

Table 3-23. ESTIMATED NO_x EMISSIONS FROM KILNS IN UNITED STATES, 1967

Process unit	NO_x, Mkg	Percent of total
Cement kilns	98	0.8
Lime kilns	19	0.15
Ceramic kilns	19	0.15
Total	136	1.1

Table 3-24. ESTIMATED NO_2 EMISSIONS IN THE BRD 1971, BASED ON FUEL CONSUMPTION

Process unit	Equivalent heating value, TJ	NO_2 emission, Mkg/hr
Cement kilns	160 000	53.5
Lime kilns	49 500	13.7
Ceramic kilns	24 200	7.6

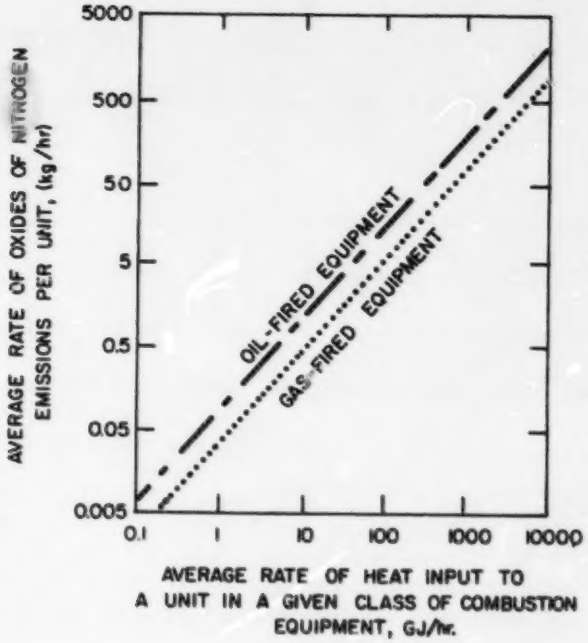

Figure 3-20. Estimation of average unit oxides of nitrogen emissions from similar combustion equipment.[86]

Continuous tank furnaces have a holding capacity of up to 1.27 Mkg and a daily output of up to 0.27 Mkg. Figure 3-21 is a cutaway view of a typical side-port, regenerative furnace.[88] It is representative of container and specialty glass furnaces: the batch feed introduced at the left, or "melting end," is heated by direct radiation from the flames and the refractory melter crown; as the mass fuses, it passes into the "fining zone" and finally through the submerged throat of the bridgewall into the "working zone." The combustion gases from the melting zone retain a considerable amount of heat, which is reclaimed in a regenerator or brick checker chamber. When the firing cycle reverses, combustion air is preheated as it passes through the brickwork. Preheating saves fuel and increases the flame temperature.

A variation on side-port is the end-port furnace, in which a single burner replaces multiple burners at one end of the tank. The type of firing possibly influences NO_x emission. The combustion gases follow a U-shaped path and enter a checker chamber for heat reclamation; reversal of the cycle is similar to that in side-port firing. Numerous variations on construction and firing include direct firing and regenerative emission with end-point firing.

Flue gas from glass-melting tanks is the major source of NO_x emissions in the glass-manufacturing industry. Operation of these tanks is similar to that of open-hearth furnaces used in steelmaking; regenerative checkerwork sets absorb heat from the combustion gases for subsequent release to the incoming combustion air. This is accomplished by a reversing valve which alternately puts each checkerwork set through its heating and cooling cycle. The sequence of intense high-temperature combustion and

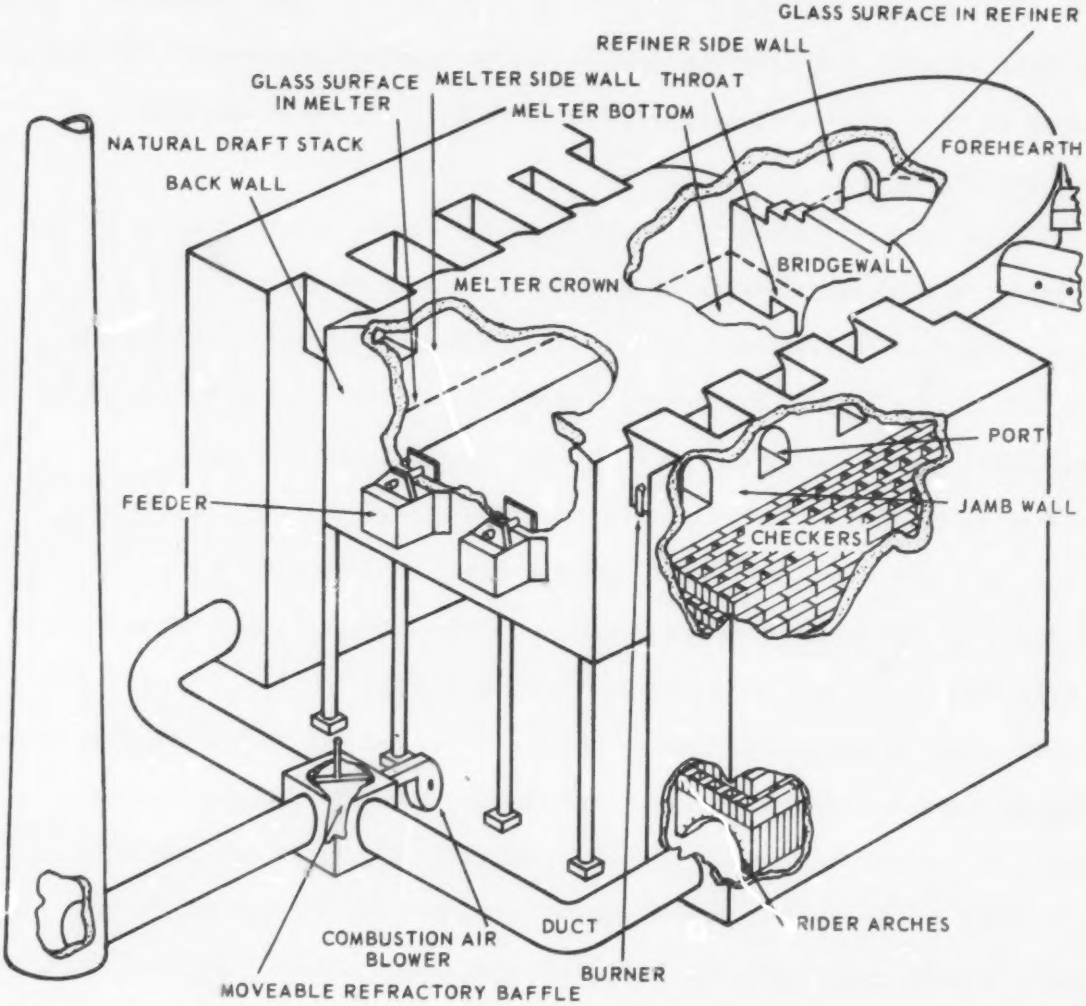
GLASS SURFACE IN REFINER
REFINER SIDE WALL
GLASS SURFACE IN MELTER
MELTER SIDE WALL
THROAT
MELTER BOTTOM
NATURAL DRAFT STACK
FOREHEARTH
BACK WALL
BRIDGEWALL
MELTER CROWN
PORT
FEEDER
JAMB WALL
CHECKERS
RIDER ARCHES
DUCT
COMBUSTION AIR BLOWER
BURNER
MOVEABLE REFRACTORY BAFFLE

Figure 3-21. Regenerative side port of glass-melting furnace.

quenching can increase NO_x emission levels up to five times those experienced in a boiler of equivalent heat release. This observation is based on measured NO_x emissions of 0.373 nkg/J for tanks firing and average of 40 GJ/hr of gas,[67] compared to 59.0 pkg/J input for normal combustion equipment of this size (see Fig. 3-17). Normal combustion supplies the lesser amounts of heat used in glass annealing and tempering, which are only minor sources of NO_x.

NO_x emissions from the United States glass industry were roughly 100 Mkg for 1967, or 1.3 percent of total NO_x, based on fuel usage in 1962[89] and glass production for 1962 and 1967.[90] In the BRD the glass production was about 3.2 Gkg in 1970. The energy consumption (1971)[91] is given in Table 3-25. A 272 000 kg/day glass melter, currently the largest, produces about 97 GJ/hr and discharges about 36.2 kg/hr of NO_x, based on an emission factor of 0.373 Mkg/J. This factor is from tests in Los Angeles, California,on glass-meter stack gas containing NO_x concentrations ranging from 435 to 1 320 ppm, with an average of 570 ppm.[66]

The type of furnace and firing shown in Fig. 3-21 is similar to that used in producing steel by the open-hearth furnace. Chemical analyses of the stack gas from an open-hearth furnace fired with 70 percent gas and 30 percent oil varied from 500 to 800 ppm of NO_x, with an average of 700 ppm. Similar results were found for four glass furnaces: 435 to 1 320 ppm, with an average of 570 ppm.[67] Other analyses of exhaust gases from a large, regenerative, gas-fired furnace showed 137 ppm of NO_x when amber glass was melted and 725 ppm when flint glass was melted.[88]

3.3.7 Miscellaneous Emission Sources

3.3.7.1 Refractory Fibers Production--The production of fibers such as mineral and glass wool requires the melting of refractory material 422 K

Table 3-25. ENERGY CONSUMPTION, BRD (1971)[91]

Fuel type	Amount consumed	Equivalent heating value, TJ	Percent
Coal	7 Mkg	200	--
Oil			
Distillate	278 Mkg	11 700	14
Residual	763 Mkg	31 800	39
Natural gas	746×10^6 m^3	26 000	40
Sewer gas	346×10^6 m^3	6 300	
Current	$1\ 590 \times 10^6$ kWh	5 700	7
Total		81 500	100

During passage through a blast of superheated steam or hot air, the flying molten globules develop and trail long fibrous tails.[92] These are assembled into batts and used for insulation. About 3.60 to 4.50 Mkg/yr of alumina-silica fibers are produced.[93] No specific data are available on the NO_x emitted during fiber production.

3.3.7.2 Perlite Expanding Furnaces--Perlite is a glassy volcanic rock. When it is heated rapidly, the water in its spherules causes it to expand into a white cellular low density material.[94] In 1967, some 324 Mkg of expanded perlite were produced,[95] of which roughly 90 percent was used as an aggregate in plaster and concrete. Essentially all furnaces are heated with natural gas and require temperatures of 1 020 to 1 254 K. In one furnace, 19 ppm of NO_x was found in the exhaust gases.[96]

3.3.7.3 Baking and Drying Ovens--Bakery ovens, sand core ovens for foundries, paint-baking ovens, plastic-curing ovens, and rock wool drying ovens[97] may be either direct-fired (combustion products contact the material being heated) or indirect-fired (heated air is circulated through the oven). Although some are oil-fired, gas-firing is most often used. Combustion air need not be preheated since operating temperatures range from 350 to 610 K. Combustion gases are discharged directly to the atmosphere unless they contain products that require an afterburner. Although a relatively large number of such ovens are in use, their average heat requirement of about 13 GJ/hr is low. NO_x stack emissions have been reported as 10 to 40 ppm.[96]

3.3.7.4 Spray Dryers--The detergent industry is a large user of spray dryers. In spray drying, a highly dispersed liquid contacts a high-temperature gas either from a direct-fired gas or oil heater or from indirect heating if a controlled atmosphere is necessary. A cyclone separator or a baghouse is frequently used to separate the dried product from the hot gases.[98] The heat requirement is about 16 GJ/hr and the NO_x in the stack gas has been reported as about 7 ppm.[96]

3.3.7.5 Welding Operations--The high temperatures involved in electric arc and oxyacetylene welding (2 200 K) favor NO_x production. With restricted ventilation, amounts of NO_x at a distance of 150 mm from the arc[99] vary from a trace to nearly 35 ppm, depending on the operation and the conditions. It is estimated that welding operations in the United States contribute roughly 63 500 kg/yr of NO_x to the atmospheric burden. This estimate is based on three assumptions: that the mean gas flow in all welding is 4.7 dm^3/s, that the concentration of NO_x is 10 ppm, and that data from Los Angeles, California,are representative of the United States.

3.3.7.6 Electrostatic Precipitators—Electrostatic precipitators have a series of high-voltage electrodes (20 000 to 100 000 volts in single-stage) which create a corona discharge that ionizes gas molecules and charges particles passing through the field. Charged particles migrate to oppositely charged surfaces and are removed from the gas stream. It is suggested that the corona discharge forms ozone and atomic oxygen, which can react with nitrogen to form NO_x. Data from precipitators tied to coal-fired boilers indicate that NO_x formation does occur; other equally acceptable data show a decrease in NO_x. This disagreement has not been resolved and needs further research. Until more reliable information is available, electrostatic precipitators cannot be considered contributors to NO_x.

3.3.7.7 High-Level Exposure in Agriculture--The NO_2 is formed in silos in the first few days after filling[100] by anaerobic bacterial action in the green fodder. Sufficient quantities (probably in excess of 40 ppm) are produced to impart color; thus, silage gas can contain high local NO_x concentrations.

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4. CONTROL TECHNIQUES

During the combustion of fossil fuels in air, nitrogen oxides (NO_x) are produced if sufficient energy is supplied to break the chemical bonds. Dissociation energies of the nitrogen-nitrogen bonds of atmospheric nitrogen are higher than those of the carbon-nitrogen bonds of fuel nitrogen--942 kJ/mol versus 251 to 628 kJ/mol, respectively. At high temperatures (1 800 K) both fuel nitrogen and atmospheric nitrogen are sources of NO_x. Thus, at lower combustion temperatures, fuel nitrogen is the predominant source of NO_x in the product gases; whereas at higher temperatures, atmospheric nitrogen is more predominant. It is estimated that 75% and 60% of the NO_x from coal and oil, respectively, result from the oxidation of fuel nitrogen. The importance of atmospheric nitrogen in contributing to pollution is illustrated by the fact that 1 000 ppm NO_x has been found in the flue gas of a high-temperature boiler using natural gas that is virtually free of nitrogen. Boiler and furnace designs are major factors responsible for the high NO_x production in the combustion of natural gas.

4.1 COMBUSTION PROCESS MODIFICATION

High combustion temperatures favor not only the oxidation of atmosphe nitrogen and fuel nitrogen but also the formation of nitrogen oxide (NO) ov nitrogen dioxide (NO_2). Once formed, NO is extremely stable, and trace concentrations are difficult to remove from a gas. Table 4-1 presents calcula equilibrium concentrations of NO_x in air and in flue gas.

In stack gas, the concentration of NO is normally less than the equilibrium concentrations at flame temperature but greater than the equilibriu concentrations at stack gas temperature. This is caused by the fact that NO_x production, which is more strongly controlled kinetically than thermodynamically, depends on the time-temperature history rather than the peak

Table 4-1. CALCULATED EQUILIBRIUM CONCENTRATION OF NITROGEN OXIDES[a] (ppm)[1]

Temperature, K	Air		Flue gas[b]	
	NO	NO_2	NO	NO_2
300	3.4×10^{-10}	2.1×10^{-4}	1.1×10^{-10}	3.3×10^{-5}
800	2.3	0.71	0.77	0.11
1 400	800	5.6	250	0.87
1 870	6 100	12	2 000	1.8

[a] For the reactions: $N_2 + O_2 \rightleftarrows 2\ NO$ and $2NO + O_2 \rightleftarrows 2\ NO_2$.

[b] 3.3 percent O_2, 76 percent N_2 in flue gas.

Table 4-2. COMPARISON OF NO_x EMISSIONS FROM COAL, OIL AND GAS ON EQUIVALENT-HEAT BASIS[3]

Fuel	Equivalent heat value	Average NO_x emissions in boilers and power plants, pkg/J		
		Household and commercial	Industry	Electric generation
Natural gas	38.9 MJ/m^3	47	88	160
Fuel oil	41.5 GJ/m^3	34-206	206	292
Coal	27.6 MJ/kg	145	362	362

Table 4-3. COMPARISON OF FUELS CONSUMED BY VARIOUS ACTIVITIES, BRD (TJ)

Fuel	Household	[a] Industry[a] Includes industrial electric generation	Utility electric generation
Gas[4]	0.168	0.921	0.197
Oil[5]	1.508	1.508[b]	0.226
Bituminous coal[6]	0.377	1.633	0.838
Lignite[6]	0.209	0.126	0.628

[a] Includes industrial electric generation.

[b] Includes refinery consumption.

or final temperatures of the combustion products. Evidence indicates that nitrogen oxidation initiated at the peak combustion temperatures is quenched by stack gas cooling prior to completion of the reaction. Consequently, relatively simple techniques aimed at reducing peak flame temperatures have reduced NO_x emissions by about 50 percent. Because of the relative simplicity of NO_x control through combustion modifications, such techniques could be the least expensive and most applicable for many types of combustion equipment.

Figure 4-1 shows theoretical concentrations of NO based on typical fuel analyses, excess air conditions, and a residence time of 0.5 second.[2] At high temperatures (e.g., in the flame zone), appreciable NO is formed; below 1 810 K, formation from fixation of atmospheric nitrogen, formation is negligible. Important keys to reducing NO_x emissions, therefore, are lowering the peak flame temperature, altering the time-temperature profile in the furnace, and reducing the availability of oxygen and nitrogen for reaction.

4.1.1 Fuel Substitution

Table 4-2 illustrates the variations in NO_x emissions by fuel type. Emissions from coal are highest; those from fuel oil are next; and those from gas firing are lowest. Consumption of various fuels in the BRD is shown in Table 4-3. However, recent experience in the electric power generation industry in California has shown that emissions from natural gas can be substantially higher than from fuel oil, particularly for large boilers. Other observations indicate that burning fuel with the lowest nitrogen content reduces NO_x emissions approximately 50 percent less than those obtained with a "high sulfur" fuel oil of relatively high nitrogen content.[7]

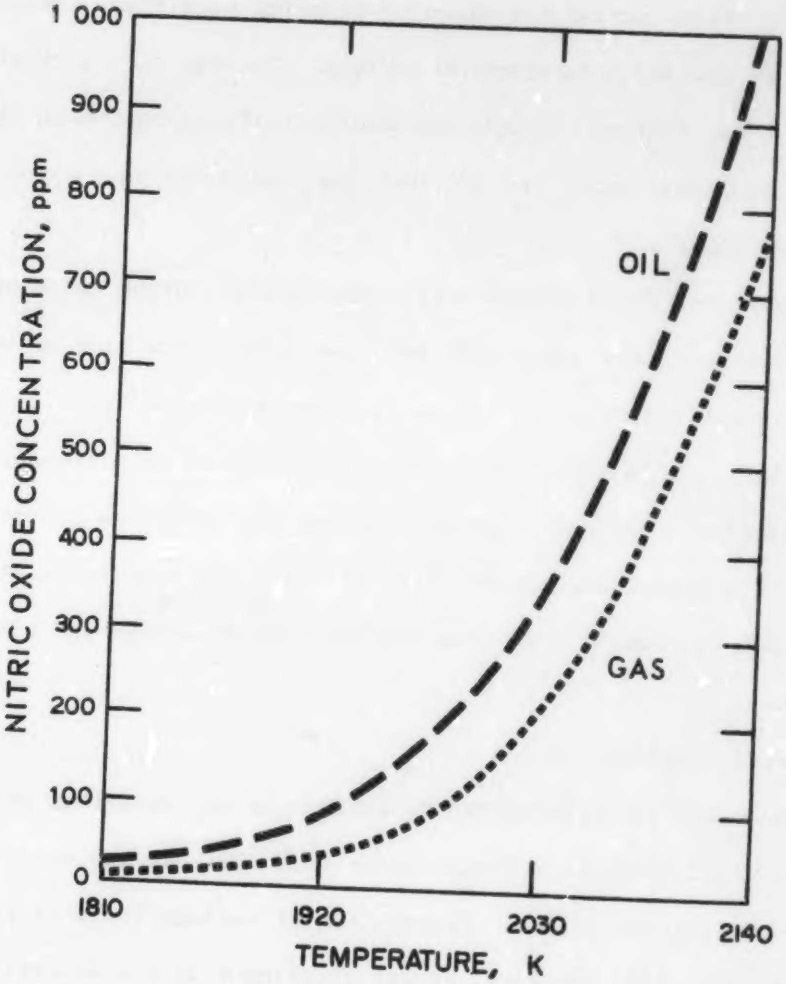

Figure 4-1. Calculated nitric oxide concentration from oil- and gas-firing (0.5 second residence time; excess air).

There are some indications that increasing fuel API gravity (i.e., decreasing specific gravity) will decrease NO_x emissions from diesel engines (Table 4-4). NO_x production decreases about 25 percent when the gravity of the fuel is increased from 30.9° to 42.8° API. This trend is supported by the low emissions obtained with natural gas. The gravity increases are accompanied by changes in fuel properties that affect the boiling range, viscosity, and cetane number. Fuel properties such as nitrogen content carbon-to-hydrogen ration, ash and metals content may also be important, but the effects of these remain to be defined. Thus, it may be possible to modify NO_x emissions by tailoring fuel properties. However, the use of special fuels adds to fuel costs because of problems with availability, refining, and marketing.

Techniques used to convert from one type of fuel to another can lead to other changes which could increase emissions. On the other hand, conversion offers an opportunity for incorporating other techniques for reducing NO_x emissions: the proper location, spacing, and design of burners to assure the lowest heat release possible, to minimize flame temperature, to minimize excess air requirements, and to provide for recirculating a portion of the flue gases back to the flame zone.

Fuel substitution as a means of reducing NO_x emissions is applicable to almost all combustion processes using fossil fuels. It is especially applicable to power plant boilers, oil-burning stationary piston engines, and domestic and commercial heating units. For small combustion processes, conversion may not be the most cost-effective method; fuel prices and availability vary widely with geographical location, user category, quantity to be used, etc., and these must be taken into consideration before fuel conversion is implemented. Widespread substitutions would adversely

Table 4-4. EFFECT OF FUEL TYPE OF EMISSIONS OF NO_x FROM STATIONARY DIESEL ENGINE[a]

°API	Fuel characteristics					NO_x emissions		Reference
	FIA Anal., percent aromatics	Est. net heat. value, MJ/kg	Boiling point, K		Kinematic viscosity (10^{-6} m^2/s) 310 K			
			50% dist.	Final		kg/kg fuel	kg/GJ	
42.8	12	43.2	493	541	2.1	0.023	0.53	7
32.7	28	42.5	478	594	2.4	0.023	0.54	7
32.4	--	42.5	544	623	3.1	0.03	0.71	7
30.9	26	42.3	554	620	3.7	0.03	0.71	7
Methane	0	49.9	399	---	---	0.0056[b]	0.11	8

[a] Precombustion chamber, turbo-charged, rated speed, about 25:1 air-fuel ratio.

[b] Actual data doubled to correct for turbo-charging; data at full throttle, 72 percent Max. Indicated mean effective pressure and 72 percent stoichiometric fuel (i.e., air-fuel ratio = 24).

affect the fuel supply structure--ultimately, the availability of fuel for this purpose may be limited. (Fuel availability, price structure, and conversion are discussed in Section 4 of AP-52, Control Techniques for Sulfur Oxide Air Pollutants.)

Converting from fuel to electrical heat may control domestic NO_x emission. It transfers the problem to the big utility plant, where controls can be more effective. On the other hand, it is sometimes the most expensive source of heat energy. In 1967, there were approximately 2.5 million automatic, domestic, electric heating installations compared to 29 million gas- and coal-fired installations.[9] Electricity can be used for all space heating, cooking, hot water heating, clothes drying, etc., and it is safe and convenient. Low-pressure waste steam from large utility plants is also used in place of fossil fuels for heating and refrigeration in urban areas.

4.1.2 Flame Temperature Reduction

The amount of heat released in a furnace, the amount of cooling surface surrounding the combustion zone, and furnace loading influence the flame temperature and therefore, the fixation of atmospheric nitrogen. The relationship between combustion temperature and NO formation is illustrated by Figure 4-2. If heat release increases but heat transfer does not, both furnace temperature and NO_x formation increase. The formation of NO_x in furnaces burning high nitrogen content fuels is not influenced so greatly by heat release and removal rates. At the same heat release rates, emissions vary with the fuel type (Fig. 4-3).[2] When the furnace loading decreases (a direct result of heat release rate), NO_x formation decreases. Tests at full, one-half, and one-quarter load resulted in NO values of 300, 185, and 145 ppm, respectively.[11]

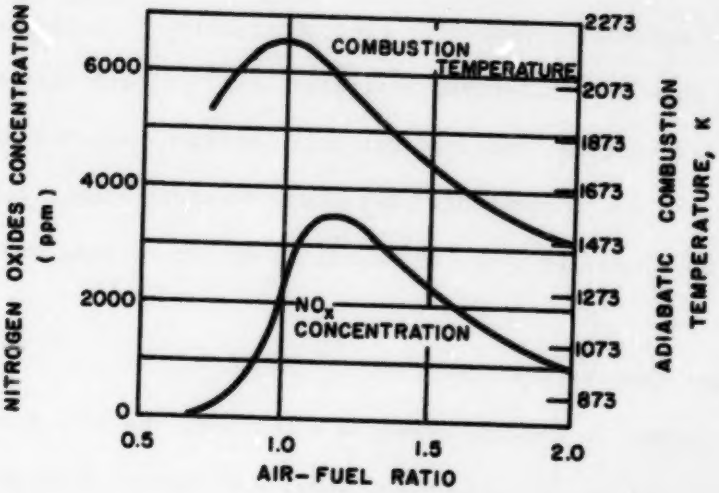

Figure 4-2. Combustion temperature and nitric oxide content (combustion of methane in air).[10]

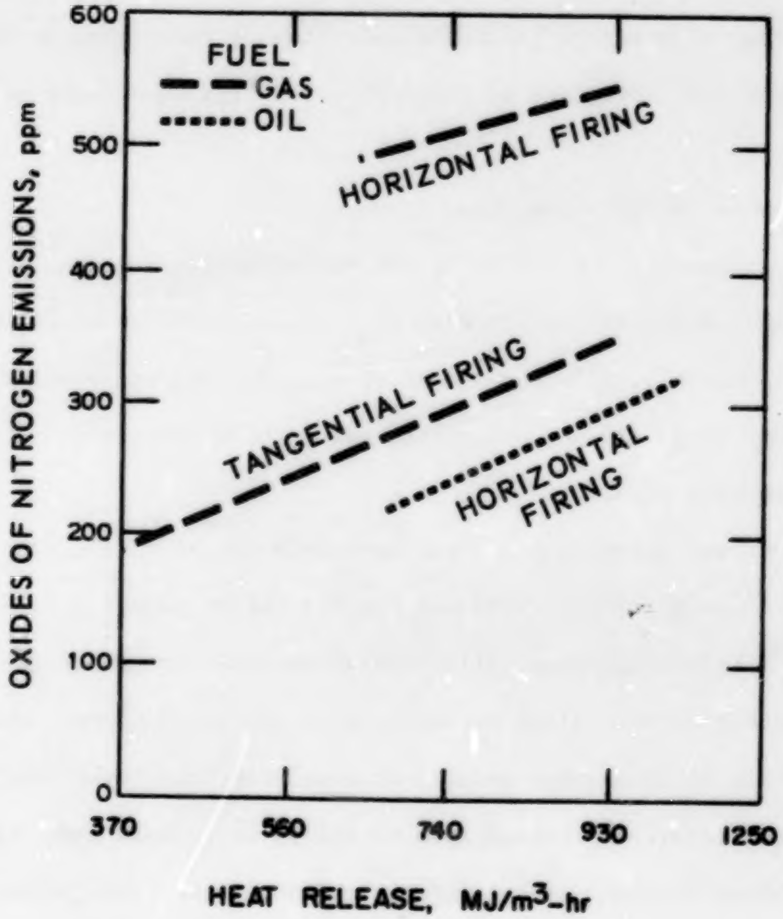

Figure 4-3. Effect of heat release on oxides of nitrogen emissions, by type of firing.

Oil flames, because of high emissivity, may lose heat by radiation more rapidly than nonluminous gas flames and thus give a lower effective residence time at peak temperatures.[12] Carburetted flames may be one way to increase the emissivity of the nearly colorless flames of natural gas. In addition, differences in the emissivities of fuel types should be evaluated so that full advantage of lower NO_x producing tendencies may be realized.

4.1.3 Low-Excess-Air Combustion

Low-excess-air combustion is one of the most promising, universally applicable techniques for reducing NO_x. This technique supplies, as nearly as possible, only the amount of air required for complete burnout of the fuel (e.g., 10 percent excess air with 90 percent stoichiometric air through the burners).

Low-excess-air combustion was developed in the United Kingdom to overcome low-temperature corrosion and air heater plugging in oil-fired boilers.[8] Later, European boiler operators made further refinements which reduced furnace slagging and heating-surface fouling. In the early 1960's, this technique was adopted at some oil-fired power stations in the United States. Investigations on oil-fired boilers have shown that NO_x emissions decrease as the oxygen content of the flue gas is reduced, even at high levels of excess air.[2] Reductions of 36 percent in a horizontally fired boiler and 28 percent in a tangentially fired unit were obtained as flue gas oxygen content was decreased about 4.0 to 2.0 percent (Fig. 4-4). Another report illustrates the magnitude of NO_x reductions possible in oil-fired boilers operating with low excess air (Fig. 4-5),[13] and similar effects were observed in laboratory tests of an oil-fired domestic heating unit[14] with a level of excess air much higher than that in the large utility boilers.

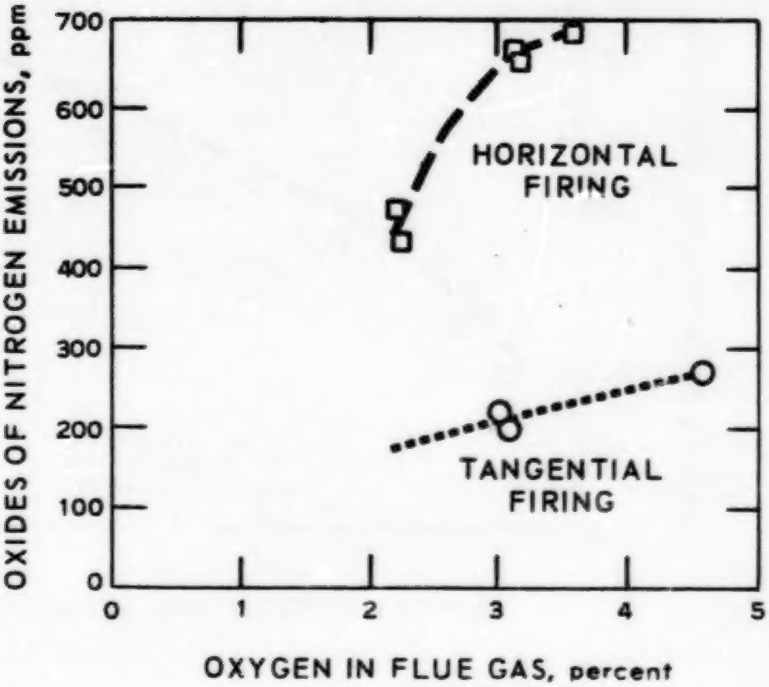

Figure 4-4. Effect of excess air on oxides of nitrogen emissions from oil-fired boilers.[2]

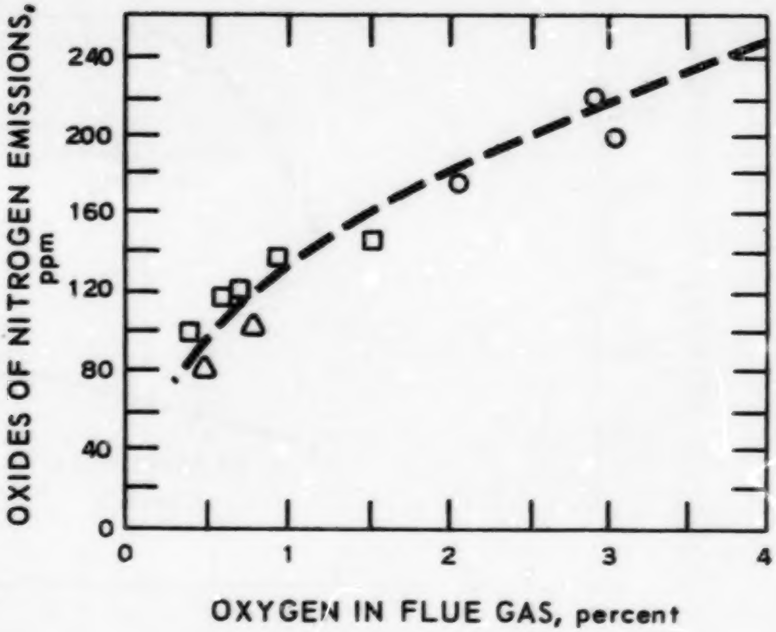

Figure 4-5. Oxides of nitrogen emissions from oil-fired boilers at low excess air.[13]

Laboratory data on coal combustion[15] indicate that both low-excess-air and two-stage combustion reduce NO_x emissions. Feeding 22 to 50 percent less excess air to the primary combustion zone reduced NO_x by 62 percent, and injection of an additional 17 percent of air just beyond the flame front improved the carbon combustion efficiency from 98 to 99.2 percent with the same reduction in NO_x.

Low excess-air requires a reasonable uniformity of air-fuel ratios in all burners to avoid unburned fuel. With pulverized coal, balance between primary air and coal streams in individual burners and balance in the mixing of these streams with secondary air at the burner are difficult to achieve. For the gas- and oil-fired packaged boiler, the combustion modifications may reduce NO_x emissions by 30 to 50 percent. Since coal-fired units are usually multiburner and gas- and oil-fired package units are usually single burner, direct comparison is difficult. A combination of flue gas recirculation and low-excess-air firing may eliminate smoke and reduce NO_x emissions by 60 to 70 percent.

Low-excess-air firing requires that burners be redesigned and that additional instrumentation be supplied for closer control of the air-fuel ratio in correspondence with load modulation. Burner redesign is relatively simple if only minor modifications are required.

Use of low excess-air increases the production of carbon monoxide (CO) and hydrocarbons and increases flame temperature in the furnace, which can promote slagging and corrosion of furnace tubes in coal-fired units and reduce operational safety. A small amount of steam or water injections can possibly control the problem of flame temperature; however, it will worsen CO and hydrocarbon problems. Special control equipment and careful supervision are required to avoid explosions, carbon monoxide, smoke, and unburned fuel emissions.

Due to the simplicity of low excess-air as an NO_x emission control technique, it is one of the most promising for many applications. In power generation stations, applications have reduced NO_x emissions by 30 to 60 percent depending on the level of excess air, the boiler design, and the type of firing.[16-18] The combination of reducing excess air and eliminating firing in the top eight burners in two 750-megawatt boilers at the Pacific Gas and Electric Company's Moss Landing Power Station reduced NO_x by about 90 percent--from 1 500 ppm to an average of 175 ppm.[19] Substoichiometric air was supplied to the bottom of 40 burners, and the top eight burners were used as ports to supply air for complete burnout.

Following small-scale laboratory demonstration of low-excess-air combustion technology, low excess-air has been used successfully on some coal-fired boilers. The importance of coal as a fossil fuel of low-excess-air firing in incinerators shows promise for significantly reducing NO_x emissions from this source.[20]

4.1.4 Flue Gas Recirculation

When a portion of the flue gas (10 to 20 percent of the furnace feed) is recirculated into the combustion zone, the reduction of NO_x emissions is attributed to the decreased flame temperature and to the dilution of the oxygen available in the flame zone.[14]

Flue gas recirculation is effective in suppressing NO_x emissions from several types of installations: in a utility boiler, reductions of about 20 percent were reported when the flue gas was reinjected through ports in the bottom of the furnace; in an oil-fired domestic heating furnace, reductions of 70 percent were obtained by recycling 50 percent of the flue gas;[13] in a test installation using domestic heating oil, reductions of 50 to 65 percent were achieved by mixing recirculated flue gas with the combustion air before combustion;[21] reductions up to 80 percent (Fig. 4-6) can be achieved by reducing excess air from 50 to 20 percent and recirculating 50 volume percent of the flue gas. On a mass basis, practical and flame stability considerations limit flue gas circulation to 20 to 30 percent of the mass of combustion air plus the mass of fuel burned. The effectiveness of NO_x reduction when gas recirculation was applied to low-temperature industrial furnaces and to vertical shaft lime kilns to control temperatures is not known; further investigation is warranted. Gas recirculation for boiler tube temperature control is not effective because the recirculated gases are injected down-stream of the burners; gases must enter the combustion zone directly.

Exhaust recycle, an effective means of controlling NO_x emissions in gasoline engines,[22] may reduce NO_x from diesel engines if the fresh air-to-fuel ratio is held constant, but further testing is needed to confirm this. It may decrease the maximum power capability of the engine and may moderately increase the cost, since additional piping and a control mechanism are required. In an internal combustion engine, an 80- to 85-percent reduction was achieved at the expense of operability,[12,23]

4.1.5 Steam and Water Injection

Flame temperature, an important parameter affecting NO_x production, can be decreased by steam or water injection. Water injection is very effective in suppressing NO_x emissions from an internal combustion engine,[24] and it is a promising potential for the intake manifold of gas engines.

Steam injection is primarily applicable to gas- and distillate-oil-fired boilers; it should not be considered for coal and residual oil boilers at this time.

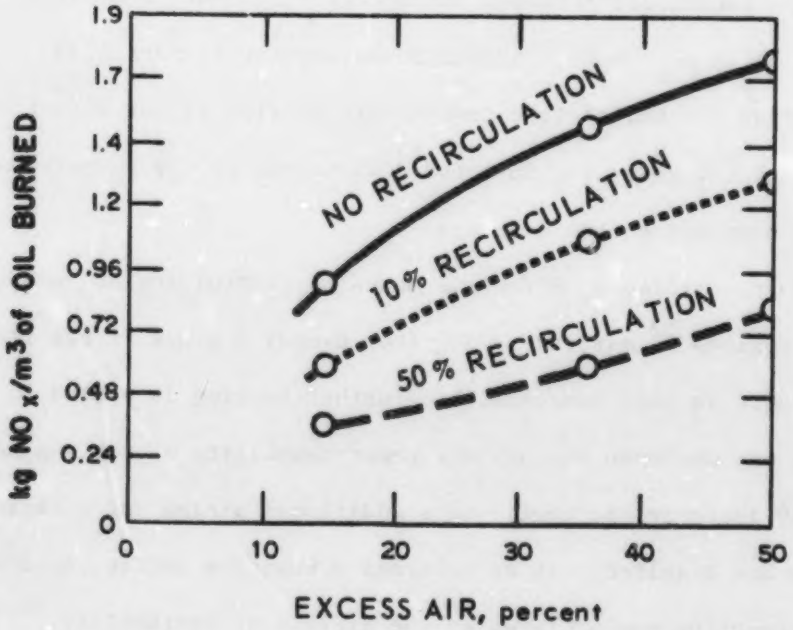

Figure 4-6. Combined effect of flue gas recirculation and excess air on oxides of nitrogen emissions from an oil-fired domestic heating furnace.[14]

In gas- or distillate oil-fired boilers, the atomizer is a simple way to inject steam; in other installations, special injection equipment must be designed for a specific degree of atomization and mixing, for the optimum point of injection, and for the required quantities of water or steam.

Water of steam injection will cause decreased efficiency and higher corrosion rates; these problems should not be neglected.

For large utility boilers, steam or water injection has not been demonstrated. Work on steam injection to control NO_x emissions from taugential boilers and stationary gas turbines has been reported.[25] The quantities of steam or water required to obtain a significant reduction in NO_x may make this application unrealistic and uneconomical, but moderate quantities used with other combustion control modifications may prove reasonable and helpful for trimming peak temperatures.

4.1.6 Two-Stage Combustion

Two-stage combustion was developed in California in the late 1950's and is being used in a number of Los Angeles County power stations. About 85 to 95 percent of the stoichiometric air is admitted to the flame through the burner throat; the remainder is injected through ports above the burner to complete the combustion; reductions of 30 to 47 percent in NO_x emissions are observed.[26] Two-stage combustion reduces NO_x emissions by several mechanisms: first, there is a lack of available oxygen for NO_x formation when the first stage is operated under substoichiometric air conditions; second, the flame temperature is lower under these conditions than in normal combustion; third, to the degree that heat is removed between stages, the maximum flame temperature in the second stage is lower than that for one-stage combustion; and fourth, the effective residence time for NO_x formation at the peak temperatures reached in the second stage is lower than for single stage combustion.

This NO_x reduction technique has been applied successfully to oil-, gas-, and coal-fired boilers. However, certain engineering problems should be noted. The combustion process is delayed, and unburned fuel losses may increase to a point where efficiency is impaired and the process becomes uneconomical. Also, in some small packaged boilers, compact size and small combustion space may make two-stage combustion impractical.

Because of the effects of two-stage combustion, the extension to multi-stage combustion for improved NO_x emission control should be considered. The staged injection of the fuel instead of the air may also result in a time-temperature-concentration profile favoring low NO_x emissions and should be investigated.

4.1.7 Burner Modifications

Burner spacing and location are important. Closely spaced burners increase flame temperature and cause greater NO_x emissions. The spacing effect is illustrated in larger boilers with many burners.

Relative to spacing and location, tangential firing is useful in reducing NO_x formation. Burners located in the corners fire on a tangent to a circle at the center of the furnace; thus, flames from individual burners have little opportunity to interact with one another so they radiate efficiently to surrounding surfaces. Tangential firing reduces NO_x up to 50 percent compared with front or opposed fired furnaces.[13] This effect may be exploited for NO_x control in other types of combustion processes. In electric power plant boilers, tangential firing was found to produce from 30 to 40 percent less NO_x[16,27]

Burner type can also be important, since some types of burners produce greater NO_x emissions than others; for example, the spud-type produces more than the radial-spud type, which in turn produces more than the ring type (Figs. 4-7, 4-8).[12] The spray angle of oil atomizers can also affect NO_x emissions; narrow spray angles are poor atomizers but produce low NO_x emissions.[12]

Turbulence reduction within the flame zone also reduces NO_x emissions. In field tests of highly turbulent vortex burners, adjustments to decrease turbulence reduced NO_x emissions by 40 percent but resulted in unsatisfactory flame conditions. On the other hand, throttling to increase windbox pressure and turbulence increased NO_x emissions by more than 15 percent.[12] Tall "lazy" flames produce less NO_x than the short, intense flames that are usually desirable for combustion.

Other modifications that may influence NO_x emissions and require further investigation include the use of turbulence chambers, as used in engines manufactured by International Harvester, Waukesha, John Deere, and "energy cells," as used in Minneapolis-Moline engines. Energy cells provide controlled combustion to prevent high peak pressures and rough operation.

The effectiveness and applicability of NO_x control through combustion modifications to industrial and commercial boilers will, in general, follow the same pattern as discussed above for public utility power plant boilers, especially when these units are large and comparable in design and configuration to the electric utility boilers. Since commercial and industrial boilers are normally smaller in size, however, the cost of installing potential controls on a unit basis could be higher. When these boilers are fired by pulverized coal, application of the techniques may also be limited, as, for example, in the case of utility units. There is reasonable assurance, however, that the suggested controls can be effective in gas- or oil-fired boilers of this category.

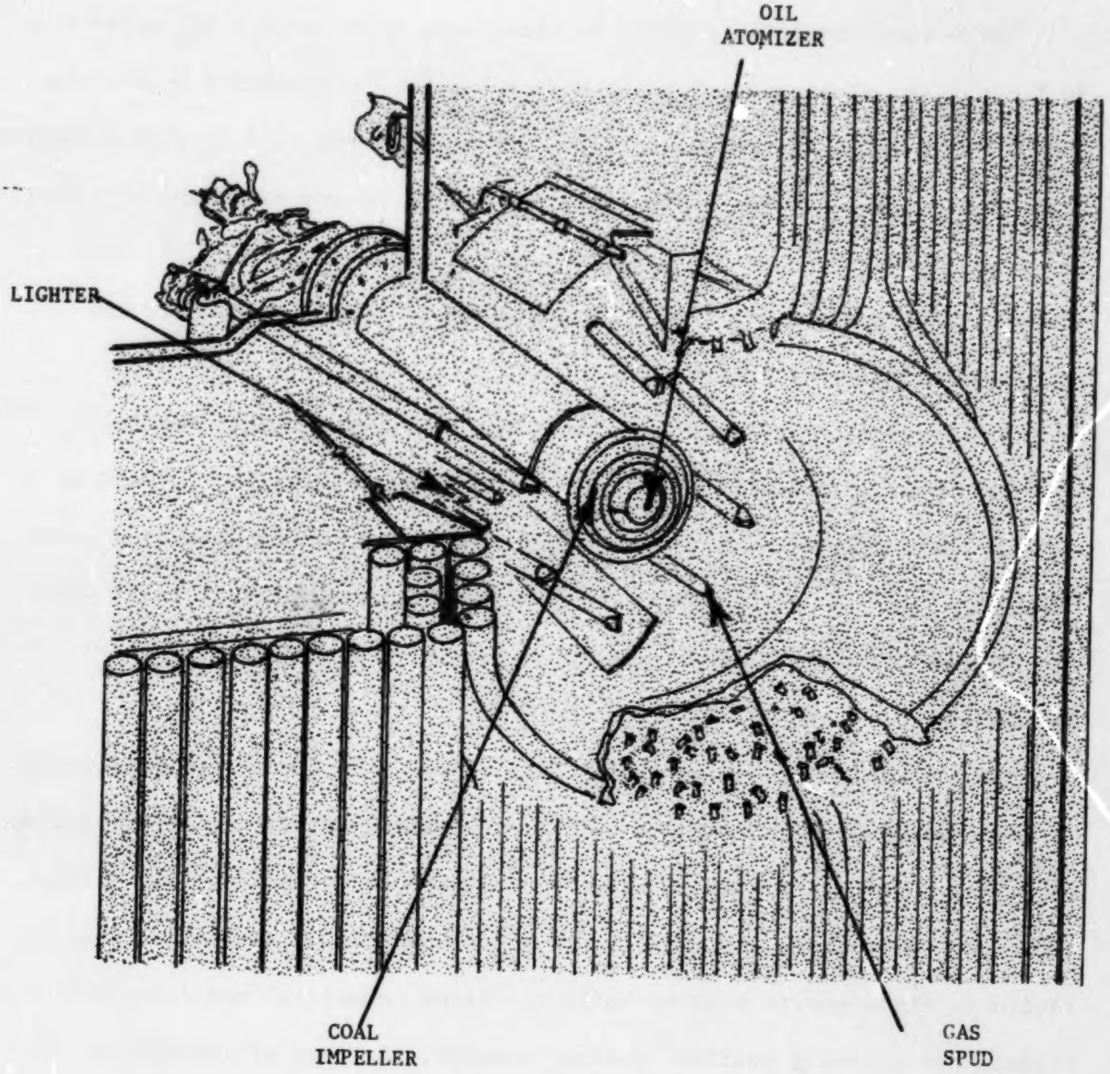
OIL ATOMIZER
LIGHTER
COAL IMPELLER
GAS SPUD

Figure 4-7. Multi-fuel burner for gas (spud-type burner), oil (circular register), and coal (circular register).

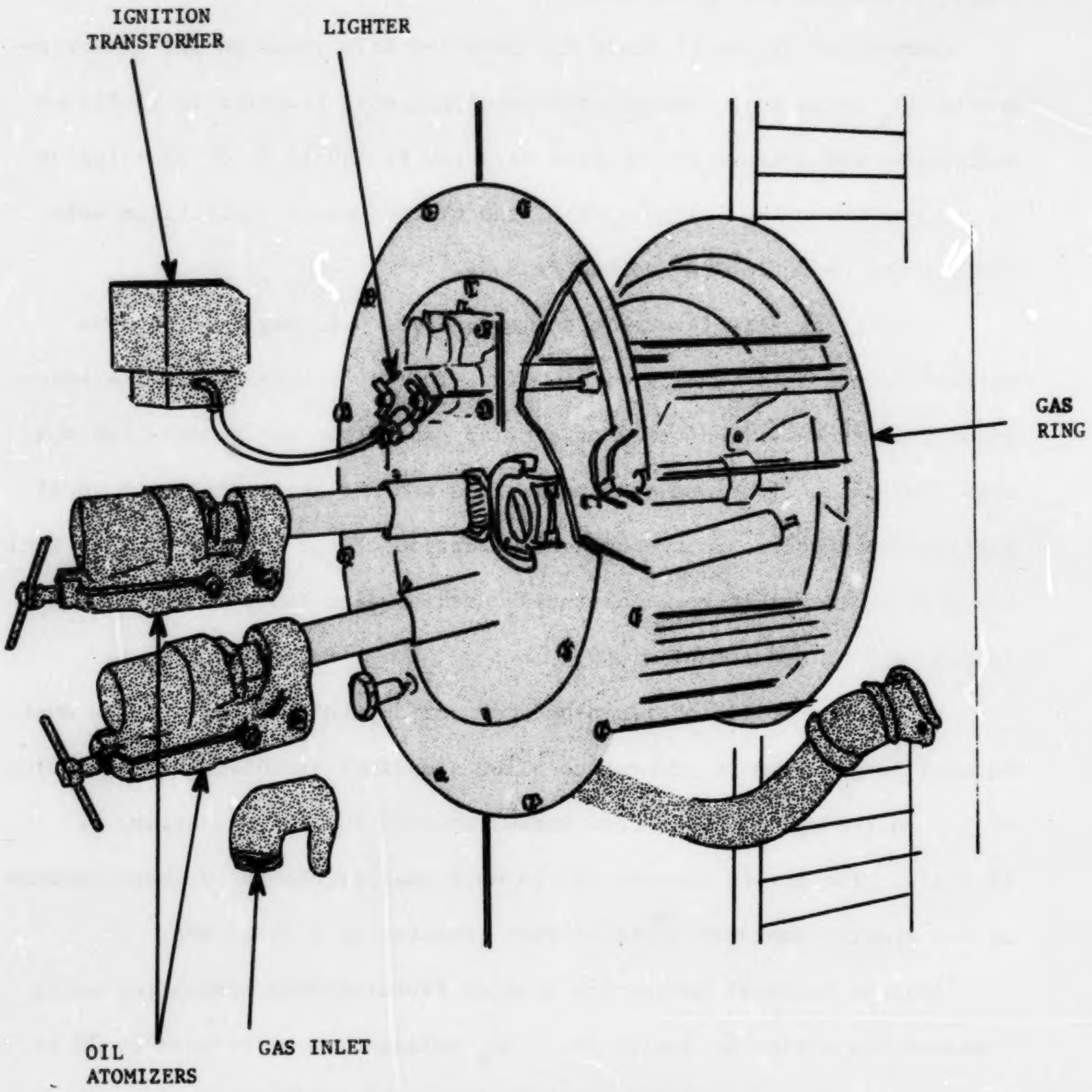
IGNITION
TRANSFORMER
LIGHTER
GAS
RING
OIL
ATOMIZERS
GAS INLET

Figure 4-8. Gas ring-type burner.

Gulf Oil Canada has announced a newly developed industrial oil burner which produces greatly reduced amounts of NO_x and other pollutants as well as offering savings in fuel, operating, and maintenance costs.[28]

4.1.8 Fluidized-Bed Combustion

Combustion of fossil fuels in fluidized beds shows potential for reducing NO_x emissions. Because the excellent heat transfer in fluidized beds keeps the average temperature very low (1 140 to 1 250 K) relative to conventional flame temperatures, the thermodynamic equilibrium suppresses the amount of NO_x formed from N_2.

In spite of this favorable outlook, about 0.13 nkg/J of NO_x was emitted from a coal-burning pilot unit. This is comparable to the emissions from stoker-fired units of similar capacity. The reasons for the high level from fluidized-bed combustions are not known, but high local surface temperatures in the bed and oxidation of the nitrogen in the fuel may both be contributors. Continuing developments may eventually result in substantial reductions of NO_x.

In boilers utilizing fluid-bed combustion, the burning section must be much larger than at present to allow a maximum fluidizing gas velocity of 1.5 to 1.8 meters per second versus present furnace velocities of 18.3 m/s. The boiler section can be much smaller than at present because of the greatly improved rates of heat transfer in a fluid bed.

Argonne National Laboratory studied fluidized-bed combustion using limestone injection to absorb SO_2. NO_x emissions were reduced by 20 to 40 percent (to 300 ppm) during coal combustion and to 80 ppm during natural gas combustion.[29,30] A system using a fluidized-bed composed of calcium sulfate in conjunction with two-stage combustion reduced NO_x emissions from 615 to 220 ppm.[31] Another fluidized-bed combustion system using natural gas and limestone injection produced NO_x emissions of only 60 to 90 ppm.[32]

4.1.9 Oxygen Enrichment

Oxygen enrichment is becoming increasingly more practical due to the decreasing cost of pure oxygen. To boost furnace capacity in the glass industry, oxygen addition is sometimes cheaper than electrical heating. Pure oxygen gives a higher flame temperature which produces more, not less, NO_x until the oxygen supply is so pure that there is not enough N_2 left in the flame to produce NO_x. Commercial oxygen (70 percent O_2 and 30 percent N_2) is not pure enough to accomplish this. If furnace operation with enriched oxygen is to become practical, it will be necessary to redesign the heat recovery system to make up for the lack of unburned nitrogen as a heat carrier; this will require substantial developmental research and the net effect on NO_x emissions is not now predictable. With pure oxygen, flame temperatures may approach 3 030 K, necessitating a change in construction materials.

4.1.10 Centralization of Energy Source

Electric boilers and central power are becoming more practical for domestic and commercial space heating as urban concentration increases. (The use of direct electric heating and the potential use of waste heat from utility power plants have already been discussed.) The application of electric boilers to steam heating, the distribution of a superheated water supply from a central power plant, and the use of a circulating heat carrier (e.g., Dowtherm) that could supply individual flash boilers in a large apartment or industrial complex are all subject to the same parameters of power costs and to the centralization of air and water pollution problems.

4.1.11 Recent Developments

Heinsohn and Becker have reported a significant reduction in NO_x emissions from combustion sources by using a premixed flat flame subjected to an electric field opposite to the direction of flow.[33]

Recent research in solid waste incinerators shows promising results. Six different "total incineration" processes in various stages of development were compared with respect to furnace type and costs.[34] In an incinerator designed by an American manufacturer as smokeless, odorless, and sootless, NO_x emissions were prevented by maintaining 670 K in the combustion room and 710 K in the stack.[35]

A magnesia-alumina fuel-oil additive was tested with the objective of reducing NO_x emissions.[36] Later experience, however, raises doubts as to its effectiveness.

4.2 GAS CLEANING

4.2.1 Flue gas

Removal of NO_x from flue gas may become the most effective control technique for those sources for which combustion modifications are either not possible or are of only limited benefit, but to date little effort has gone into research and development of this technique. The only methods now considered practical are those that remove both sulfur dioxide and NO_x, and the amount of NO_x removed is limited to about 20 percent or less of that ordinarily found in flue gas. SO_x removal is discussed in the document, AP-52, Control Techniques for Sulfur Oxide Air Pollutants.

The removal of NO_x from flue gas will continue to be more difficult than SO_2 removal[27] because NO_x exists primarily as stable NO and because compounds present in greater concentrations than the NO_x (Table 4-5)--such as water, carbon dioxide, and SO_2 from the combustion of coal, oil, and natural gas—interfere with NO_x removal. The relative reactivities of the gaseous components are suggested by solubility data. These solubility data are for pure gases in equilibrium with water, at 101 kN/m^2 pressure, whereas NO_x (particularly NO_2) are present in the flue gases in very low concentrations. Other complications arise from the need to process large volumes of flue gas for NO_x control. A modern 1 000-megawatt power plant, for example, emits about 944 m^3/s of flue gas. Processing such a large volume of hot gas presents formidable equipment and engineering problems.

At present, there are a large number of SO_2 control systems being studied, some of which have some potential for NO_x control. Of these, the limestone scrubbing process and the Reinluft Char process show some possibility for commercial application.

4.2.1.1 Limestone Wet-Scrubbing Process--Slaked lime or limestone aqueous suspensions remove SO_x (SO_2 and SO_3) as acid gases and remove some NO_2, or NO_2 plus NO. There are two basic variations of the limestone wet-scrubbing technique. In the first, dry limestone is injected directly into the boiler furnace where it reacts with 20 to 30 percent of the total SO_2 and essentially all the SO_3 ahead of a water scrubber; it is then calcined to the more reactive quicklime for use in the scrubber. In the second, limestone is added directly to the scrubber.

Although limestone is less efficient than lime in the scrubber, the second technique avoids potential boiler problems such as abnormal slagging, increased erosion, and interference with combustion and temperature control. In both cases, the solids form a reactive slurry, which combines with most of the SO_x and some of the NO_x and which must be removed from the scrubber for disposal. In some cases, the requirements of wastewater disposal may

Table 4-5. TYPICAL COMPOSITIONS AND SOLUBILITY OF STACK GASES

Component	Volume percent from combustor			Solubility in wat[illegible]/V, at 10[illegible], [illegible]
	Coal[a]	Oil[b]	Gas[c]	
N_2	76.2	77.0	72.3	0.[illegible]
CO_2	14.2	12.0	9.1	0.[illegible]
H_2O	6.0	8.0	16.8	
O_2	3.3	3.0	1.8	0.0039
SO_2	0.2	0.15	--	9.41
NO_x	← 0.07[d] →			
NO (% in NO_x)	← 90 - 95 →			0.0056
NO_2 (% in NO_x)	← 5 - 10 →			Decomposes[e]

[a] Calculated for burning with 20% excess-air a typical high volatile bituminous coal of the following composition: carbon, 70.1%; oxygen, 6.6%; hydrogen, 4.9%; nitrogen, 1.4%; sulfur, 3.0%; ash, 12.7%; H_2O, 1.3%.

[b] Calculated for burning with 20% excess-air a typical residual fuel oil of the following composition: 86.5% C, 10.3% H, 2.5% S, 0.7% N.

[c] Calculated for burning natural gas with 10% excess-air.

[d] This is an average value. Actual values range from 0.02 to 0.15%.

[e] Phase diagram in a sealed tube shows equilibrium with water at 298 K, 54 wt % N_2O_4 (or 120 g/100 g of H_2O).[37]

limit the use of limestone scrubbing processes. Scrubbing with the water slurry cools the gases to the saturation temperature of about 324 K, produces a visible and less buoyant plume, and thus gives higher ground-level concentrations.

Early work with limestone and lime scrubbing (done in England in the 1930's) was carried out with direct addition of the reactant to the scrubber. James Howden & Co., Ltd., and Imperial Chemical Industries installed lime- and chalk-scrubbing processes at the Fulham power plant in London and the Tir John power plant in Swansea. In pilot plant studies, Howden and ICI report[38] 60 to 70 percent removal of NO_x and 97 to 99 percent removal of SO_x. In the United States, UOP's study of limestone and dolomite scrubbing at Wisconsin Electric's Oak Creek power plant and Combustion Engineering's study of dry limestone injection into the boiler and wet scrubbing at Detroit Edison's St. Clair power plant[39] indicated NO_x removals averaging about 20 percent; the close agreement in results obtained by these two studies and the disparity between these and the Howden-ICI results make the earlier data suspect. Earlier data may have been complicated by difficulties in the analysis for NO_2.

Combustion Engineering has been offering its process (Fig. 4-9) commercially. The process has already been installed by Union Electric Co. at its Meramec plant, and it is being installed by Kansas Power and Light (KP&L) at its Lawrence plant. In both cases the boilers being outfitted are rated at 125 megawatts. A number of problems have been encountered with the Meramec plant unit.[40] This unit has not yet been studied with respect to NO_x removal, however.

4.2.1.2 Reinluft Char Process--The Reinluft Char process uses a slowly moving bed of activated char to remove primarily the SO_x from flue gases. Some NO_x may simultaneously be removed. This process is described in

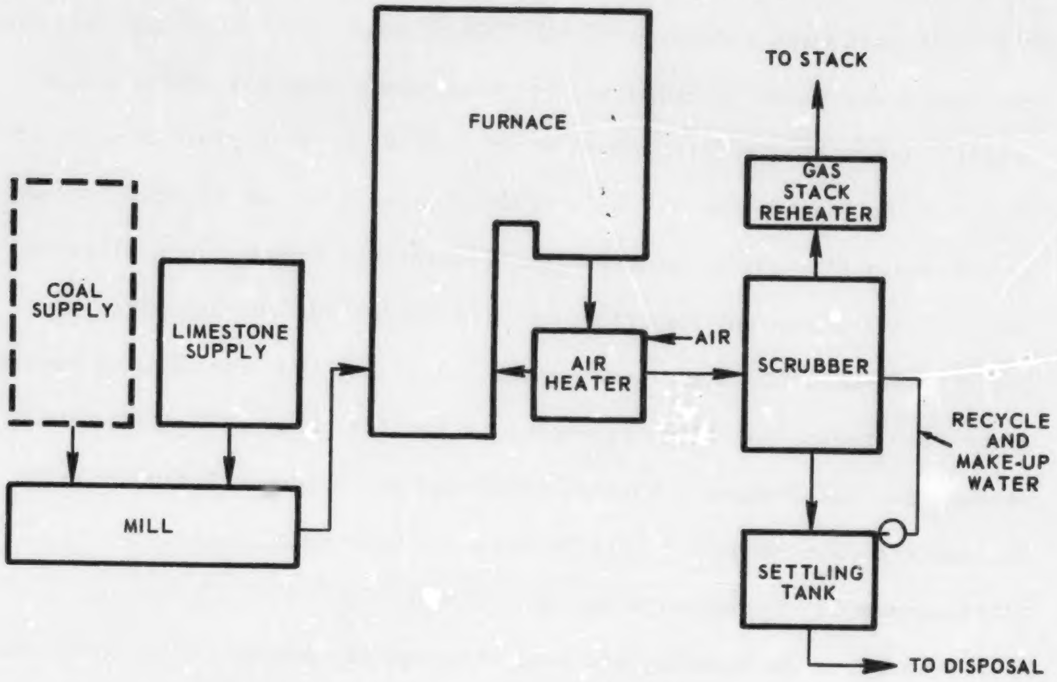
TO STACK
FURNACE
GAS STACK REHEATER
COAL SUPPLY
LIMESTONE SUPPLY
AIR
AIR HEATER
SCRUBBER
RECYCLE AND MAKE-UP WATER
MILL
SETTLING TANK
TO DISPOSAL

Figure 4-9. Limestone injection wet-scrubbing process.

Section 4.5.6 of NAPCA publication AP-52, Control Techniques for Sulfur Oxide Air Pollutants.

4.2.1.3 Other Flue Gas Cleaning Techniques--It was previously indicated that lime-water scrubbing removes about 20 percent of NO_x in the form of N_2O_3 (produced by the interaction of equal molar quantities of NO and NO_2). Removal could perhaps be improved by increasing the NO_2-NO ratio from its present flue gas value of about 0.1 to a level of 1.0. Techniques suggested[41] for achieving more optimum ratios include catalytic oxidation, homogeneous oxidation with ozone, and addition of NO_2 to the gases. In the case of NO_2 addition, part of the NO_2 might be obtained from the nitrites and nitrates formed in the scrubber by thermally decomposing these salts and oxidizing the concentration NO_x produced.

Selective reduction of NO_x by ammonia over supported platinum catalyst has been used in three nitric acid plants with very limited success. The use of noble metal catalyst restricts the application of this technique to gases containing no more than 1 ppm SO_x. Only the flue gas from gas-fired equipment could possibly meet this requirement; for other fuels, desulfurization processes cannot provide complete SO_2 removal.

The use of metal catalysts other than noble metals for the selective ammonia reduction of NO is discussed in several patents.[42-44] These catalysts are not sensitive to sulfur poisoning.[43,44] If these claims are correct, NH_3 reduction could be used in coal-, oil-, and gas-fired plants. Considerable research would be needed, however, before such a speculative system could be developed.

4.2.2 Chemical Process Offgas

The economic necessity of recovering NO_2 from the manufacture and use of nitric acid has led to chemical research of problems in NO_x control.

Most of the research has been for the recovery of about 3 000 ppm of NO_x; concentrations from stack gases are much lower.

Many techniques have been developed for treating tail gas from nitric acid plants. Catalytic reduction is commercially suited to nitric acid manufacturing, and molecular sieve adsorption is now used commercially with moisture-free gases.[45,46] Caustic scrubbing has few commercial applications because of problems in disposing of the spent caustic, and absorption in concentrated sulfuric or nitric acid does not appear to be competitive with other methods.[47]

4.2.2.1 Lime/Limestone Scrubbing--Lime-water, or a limestone slurry, can remove NO_2 or a 1:1 mol ratio of NO_2 and NO (equivalent to N_2O_3), but because this technique can create a serious problem of wastewater disposal, it is in limited use. Since the limestone-based scrubbing processes are usually associated with flue gas cleaning, more details are given in that section (4.2.1.1) of the report.

4.2.2.2 Caustic Scrubbing--In caustic scrubbing, NO_x in nitric acid tail gas reacts with sodium hydroxide, sodium carbonate, ammonium hydroxide, or calcium carbonate to form nitrite and nitrate salts. The examples of 90-percent removal of NO_x by caustic scrubbing reported in the literature[48] probably reflect a favorable NO-NO_2 ratio of about 1:1. The salts in the spent caustic solution become a serious water pollutant if released by industry as a liquid effluent, and yet the concentrations are too dilute for economic recovery.[49] Thus, this technique is not used extensively by the industry.

Caustic scrubbing is one of the more plausible controls for specialty batch nitration processes. Tests on batch operations used in dyestuff production indicated that a modified ejector scrubber was the most efficient for cleaning the offgas. The scrubber was operated at a gage pressure of 9 atmospheres and used a solution of sodium sulfite and sodium hydroxide as the wash liquid.[50]

4.2.2.3 Catalytic Reduction and Abatement--Catalytic reduction is particularly applicable to pressure processes because the reactor can be placed in the tail gas circuit after the preheater. In catalytic nonselective and selective reduction units, the fuel reduces NO_x--that is, converts NO_2 to NO and NO to N_2. In all catalytic reductions, catalyst activity decreases somewhat with use. Energy generated by the reactions is recovered in a turboexpander and provides most of the power required by the air compressor.[51,52]

Nonselective reduction units are designed either for decolorization and energy recovery or for NO_x abatement. A decolorization or power recovery unit reduces NO_x to NO by passing a preheated mixture of tail gas and methane over the catalyst, but its capacity to reduce NO to elemental nitrogen is limited:

$$CH_4 + 4NO_2 \rightarrow 4NO + CO_2 + 2H_2O \; ; \qquad (1)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \; ; \qquad (2)$$

$$CH_4 + 4NO \rightarrow 2N_2 + CO_2 + 2H_2O \, . \qquad (3)$$

(Similar equations can be written by substituting 4 moles of hydrogen for 1 mole of methane.) The kinetics reaction (1) is faster than reaction (2), and reaction (2) is much faster than reaction (3). Thus, decolorization requires just enough fuel for partial oxygen burnout; abatement requires sufficient fuel for complete oxygen burnout.

Nonselective reduction units for decolorization and power recovery are used in about 50 nitric acid plants in the United States.[49] Plants using natural gas for fuel must preheat the tail gas to about 760 K to insure ignition; for those using hydrogen, 420 K will insure ignition.[53] For both fuel types, catalytic reduction is highly exothermic: heat increase with methane is about 380 K for each percentage of oxygen burnout, and with hydrogen it is about 400 K.[2] For decolorization, the outlet temperature is ordinarily limited to 920 K--the maximum for turboexpanders with current technology.[49] Increased power recovery may justify adding sufficient methane to reach the maximum temperature.

In decolorization, supports for platinum or palladium catalysts include ceramic spheres, ceramic pellets, ceramic honeycomb, and woven nickel-chromium ribbon. The honeycomb structure gives low pressure drop at high space velocities of 100 000 volumes per hour per volume. In new decolorization units, ceramic honeycomb supports are favored over ceramic spheres and pellets that require low hourly space velocities of 30 000 volumes per hour per volume.[54-56] However, at a given level of NO_2 removal, a catalyst supported by nickel-chromium uses more fuel but converts more NO to N_2 than a ceramic-supported catalyst.[49]

Both catalyst and nitric acid manufacturers report satisfactory performance for decolorization units. Reduction of total NO_x is limited, but reduction of ground-level NO_2 concentrations in critical areas near the plants is substantial.[49]

Nonselective abatement is more difficult technically than decolorization, and commercial results are less satisfactory. Units that no longer abate NO emissions can be used for energy recovery and decolorization.[49] In nonselective abaters, the heat released in burning out all the oxygen from the tail gas must be controlled before extensive NO reduction proceeds. That is, when tail gas is preheated to 750 K to insure ignition of methane, the outlet temperature reaches 1 010 and 1 130 K for 2 and 3 percent oxygen burnouts, respectively. The maximum for turboexpanders is 922 K and the maximum for catalyst is 1 080 to 1 140 K. For single-stage operation, the oxygen cannot exceed 2.6 percent to remain within the temperature limit of the catalyst, and cooling must be provided to meet the turboexpander limit. Older turbines may have even lower temperature limitations.

Fuel requirements are 10 to 20 percent over stoichiometric for methane. Some hydrocarbons and carbon monoxides appear in treated tail gas; furthermore, not all methane is converted in decolorization. Less surplus fuel is required when hydrogen is used.[49]

Two or three plants have single-stage nonselective abaters designed for natural gas; these use ceramic sphere supports at space velocities up to 30 000 volumes per hour per volume.[49] Oxygen concentration cannot exceed 2.6 percent, and the reactors must withstand 1 080 to 1 110 K at 690 to 83 kN/m^2(gauge), which requires costly refractories or alloys. On a plant scale, the effluent gas must be cooled by heat exchange or quench to meet the temperature limit of the turbine; it would be logical to use a waste-heat boiler to generate steam. One plant maintains NO_x levels of 500 ppm or less over an extended period of time. Operation close to 300 ppm might be obtained. Catalyst suppliers report 100 ppm from small-scale tests with gas of fixed composition.

Two-stage nonselective abaters use honeycomb ceramic catalysts with space velocities of about 100 000 volumes per hour per volume in each stage.[55] In the United States, one commercial installation has two reactor stages with interstage heat removal.[56] Another preheats 70 percent of the feed to 750 K, adds fuel and adjusts it to obtain the desired outlet temperature, and passes the mixture over the first-stage catalyst. The remaining 30 percent of the tail gas, preheated to only 390 K, quenches the first-stage effluent; the two streams plus the fuel for complete reduction pass over the second-stage catalyst; and the effluent passes directly to the turboexpander. This type avoids high temperatures and the use of coolers and waste-heat boilers.[53,57,58]

Commercially, single-stage abaters have been modestly satisfactory and cheaper than two-stage units operating on natural gas. Two-stage units have achieved abatement for only a few weeks before the declining catalyst activity causes increases in NO levels. The success of single-stage abaters may be due to the reducing atmosphere for the catalysts, the high temperatures, and the use of spherical rather than honeycomb catalyst supports. The reactor in two-stage units designed for a space velocity of 100 000 volumes per hour per volume would be too small for a spherical catalyst (which effectively removes NO at a space velocity of about 30 000). The failure of the honeycomb catalyst in NO reduction compared to its success in decolorization may reflect that reaction kinetics make it much more difficult to reduce NO than NO_2.[49]

In selective abatement, ammonia reacts with NO_x in preference to molecular oxygen. Selective abatement must be carried out within the narrow range of 483 to 544 K so that ammonia will reduce NO_2 and NO to molecular nitrogen without simultaneously reacting with oxygen:

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O\ ; \tag{4}$$

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O\ . \tag{5}$$

Above 544 K, ammonia may oxidize to NO_x; below 483 K, it may form ammonium nitrate.[51]

Three commercial plants have installed selective abatement units. Performance has ranged from unsatisfactory to partly successful. The reaction supplies little energy for recovery in the turboexpander.[49]

A number of World War II vintage nitric acid plants have reciprocating compressors for power recovery. If selective abaters were installed, ammonium salts could enter the lubricating oil system and produce an explosion; this is not a problem with turboexpanders.

For selective abatement, platimun on a honeycomb support has not been successful; consequently, nitric acid manufacturers do not consider selective abatement to be commercially developed.[49] Platinum on pellets may be satisfactory,[55] but the high cost of platinum catalysts and the necessity of using them only on a gas stream that is essentially free of sulfur compounds limit the number of analogous stack gases with which they can be used.

One patented technique for recovering NO_x as usable ammonium nitrate from chemical process offgas is to adjust the mole ratio of NO and NO_2 to 1 by oxidizing or reducing NO to NO_2 or by adding NO_2 to the offgas and NO_x to an ammoniacal solution.[59]

Standard Oil Company researchers have developed a technique of catalytic reduction that reduces 98 to 100 percent of the NO_x to nitrogen and oxygen by using high-melting catalysts of alkali metal oxides, alkali metal silicates, alkaline earth metal oxides or alkaline earth metal silicates, or mixtures of these. The technique is effective over a range of 973 to 1 373 K.

4.2.2.4 Other Generally Applicable NO_x Control Techniques--Recently commercially available molecular sieves are reportedly much more effective adsorbents for NO_x in tail gas than silica gel.[45,46] (Silica gel is probably more acid resistant than zeolites.) The adsorbed NO_x, desorbed either as enriched NO_x or as nitric acid by displacement with hot air or steam, is returned to the nitric acid plant.

Sulfuric acid readily adsorbs a 50-50 mixture of NO and NO_2; however, water in the tail gas dilutes the acid, and reconcentration makes acid absorption costly. Concentrated nitric acid would absorb some NO as well as the 50-50 mixture of NO and NO_2, but again, the water in tail gas dilutes the acid; absorption by 20 to 35 percent nitric acid, followed by regeneration of the contaminated acid with oxygen, has been proposed.[47]

Emissions from storage tanks and from nitric acid concentration can be collected and returned to the process feed by a vapor recovery system constructed of stainless steel. Sorption of NO_x in chemical process off-gas by ion exchange resins shows promise and should be studied further.[60] Frequently, the emissions are disposed of by incineration, which reduces the NO_x content by 75 to 90 percent.[61] Incineration is a noncatalytic reduction technique: NO_x is reduced to N_2 when a fuel is added in at least 10-percent excess over the amount equivalent to the NO_x and oxygen present. This technique has been used successfully in organic oxidation and nitrations.

Dilution of NO_x tail gases in the stack with large volumes of air makes the effluent less visible and also increases stack velocity, which increases effective stack height and thus contributes to decreased ground-level NO_x concentrations. Total NO_x emissions are not reduced by stack dispersion but only spread over a larger area.

4.2.2.5 Specifically Applicable NO_x Control Techniques--In the glass industry, modifications for reducing flame temperatures do not appear applicable, since high flame temperatures are required to heat the charge to 1 700 to 1 830 K. Operation with excess air might lower NO_x levels while maintaining or increasing temperature but would require improved controls. Automatic controls and changes in burner positioning are potential techniques of reducing NO_x. Other control measures which may be specific for glass melting are:

1. Minimize hot spots within the furnace. Minute changes in residence time in extremely high temperature zones can considerably affect NO_x emissions (Table 4-6).
2. Use an end-fired tank that has a single large burner and a long travel path. A large, luminous flame produces less NO_x than an intense restricted flame.
3. Use electric heating as a booster to increase temperature or production. It is favored for colored glasses and tends to extend refractory life. It reduces NO_x emissions to the extent that combustible fuels have been displaced but transfers NO_x emissions to the power plant. An all-electric melter requires less capital investment than conventional melters.[63] However, the economics involved are not clearly in favor of electric heating except as a booster, since electric power is more costly than fuel in most areas, even though it is 75-percent efficient and fuel is only 15 to 20 percent.[64]

Two recent techniques for removing NO_x from coke oven gases have been described. The first uses a CO-MO catalyst in acetylene selective hydrogenation and NO_x removal. This technique reduces emissions by 33 to 99 percent depending on the original concentration of NO_x in the gas.[65] The second uses electric brush discharge filters to remove NO_x from the coke oven gas. Efficiencies up to 93 percent were reported.[66]

Table 4-6. TIME FOR NO FORMATION IN A GAS CONTAINING 75 PERCENT NITROGEN AND 3 PERCENT OXYGEN[62]

Temperature, K	Time to form 500 ppm No, sec	NO concentrations at equilibrium, ppm
1 580	1 370	550
1 810	16.2	1 380
2 030	1.10	2 600
2 250	0.117	4 150

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5. EMISSION FACTORS FOR NITROGEN OXIDE SOURCES

An emission factor is a statistical average of the rate at which pollutants are emitted from the burning (or processing) of a given quantity of material. (The factors can be based on some other meaningful parameter, such as the number of miles traveled in a vehicle.) To determine each factor, reliable data from a source or group of sources are gathered, correlated with information on process use, and tabulated. Either an average or a range of values is selected.

Some emission factors are based on limited data; others, on extensive data that are highly variable; and still others, on extensive, consistent data. It is, therefore, important that the precision of the data be evaluated before the factor is used for estimating emissions.

In general, the emission factors for nitrogen oxide air pollutants are not precise indicators for any single process even though the details of that process are known. They are more valid when applied to a number of processes.

Emission factors listed in Table 5-1 are for uncontrolled sources, except as noted in the table.

Table 5-1. - UNCONTROLLED EMISSION RATES FOR NITROGEN OXIDE SOURCES[1]

Type of Emission Source		Emission Rate (g/kg)[1]
STATIONARY FUEL COMBUSTION SOURCE		
Bituminous Coal:		
Furnace greater than 30 MJ/s		
General		9.0
Wet bottom		15.0
Dry bottom		9.0
With cyclone		27.5
Furnace from 3 to 30 MJ/s		7.5
Furnace less than 3 MJ/s		3.0
Hand-fired unit		1.5
Anthracite Coal:		
Dry bottom furnace		9.0
Overfeed stoker		
Furnace less than 3 MJ/s		3.0
Furnace greater than 3 MJ/s		7.5
Hand-fired unit		1.5
Fuel Oil:		
Power plant	kg/m^3	12.6
Industrial/commercial unit		
Residual tangentially fired	kg/m^3	4.8
Residual horizontally fired	kg/m^3	9.6
Distillate tangentially fired	kg/m^3	4.8
Distillate horizontally fired	kg/m^3	9.6
Domestic unit	kg/m^3	1.4
Natural Gas:		
Power plant	kg/1000 m^3	6.2
Industrial process boiler		
Less than 370 KW	kg/1000 m^3	1.9
Greater than 5600 KW	kg/1000 m^3	3.7
Domestic heating unit	kg/1000 m^3	0.8
Commercial heating unit	kg/1000 m^3	1.6
Gas turbine	kg/1000 m^3	3.2
Gas engine		
Oil and gas production	kg/1000 m^3	12.3
Gas plant	kg/1000 m^3	68.9
Refinery	kg/1000 m^3	70.5
Pipeline	kg/1000 m^3	116.9

See footnote at the end of the table.

UNCONTROLLED EMISSION RATES FOR NITROGEN OXIDE SOURCES--Continued

Type of Emission Source			Emission Rate (g/kg)[1]
Liquified Petroleum Gas (LPG):			
Industrial process furnace			
Butane	kg/m^3	1.45	
Propane	kg/m^3	1.35	
Domestic furnace			
Butane	kg/m^3	0.72	
Propane	kg/m^3	0.72	
Commercial furnace			
Butane	kg/m^3	1.2	
Propane	kg/m^3	1.2	
Wood and Bark			5.0
SOLID WASTE DISPOSAL			
Refuse Incinerator:			
Municipal multiple chamber			
Without settling chamber and water spray system			1.0
With settling chamber and water spray system			1.0
Industrial/commercial			
Multiple chamber			1.5
Single chamber			1.0
With control			5.0
Flue-fed			1.5
Modified flue-fed			5.0
Domestic single chamber			
Without primary burner			0.5
With primary burner			1.0
Pathological			1.5
Auto Body Incinerator:			
Uncontrolled	kg/car	0.045	
With afterburner	kg/car	0.009	
Conical Burner:			
Municipal refuse			2.5
Wood			0.5
Open Burning:			
Municipal refuse			3.0
Automobile components			2.0
Horticultural refuse			
Agricultural field burning			1.0
Landscape refuse and pruning			1.0
Wood			1.0

See footnote at the end of the table.

UNCONTROLLED EMISSION RATES FOR NITROGEN OXIDE SOURCES--Continued

Type of Emission Source		Emission Rate (g/kg)[1]
MOBILE COMBUSTION SOURCE		
Gasoline-Powered Motor Vehicles	kg/m^3	21.0
Diesel:		
Truck or bus	kg/m^3	44.3
Locomotive	kg/m^3	9.0
Aircraft:		
Turbofan		
Jumbo jet	kg/engine-LTO	2.7
Long range	kg/engine-LTO	2.3
Medium range	kg/engine-LTO	3.2
Turbojet	kg/engine-LTO	2.3
Turboprop	kg/engine-LTO	2.3
Turboshaft	kg/engine-LTO	0.27
Piston		
Transport	kg/engine-LTO	0.18
Light	kg/engine-LTO	0.09
Vessel:		
Steamship		
Underway	kg/km	1.13
In-berth	kg/day	90.7
Motor ship		
Underway	kg/km	0.34
In-berth	kg/day	22.7
CHEMICAL PROCESS INDUSTRY		
Adipic Acid Manufacture (oxidation of cyclohexanol/ cyclohexanone		6.0
Explosives Manufacture:		
TNT		
Nitration reactor		80.0
Nitric acid concentrator		0.5
Red water incinerator		3.0
Nitrocellulose		
Reactor pot		6.0
Sulfuric acid concentrator		14.5

See footnote at the end of the table.

UNCONTROLLED EMISSION RATES FOR NITROGEN OXIDE SOURCES--Continued

Type of Emission Source	Emission Rate (g/kg)[1]
Nitric Acid Manufacture:	
Ammonia oxidation	
Old plant	28.5
New plant	1.0-3.5
Nitric acid concentrator	
Old plant	2.5
New plant	0.1
Terephthalic Acid Manufacture	6.5
FOOD AND AGRICULTURAL INDUSTRY	
Coffee Roasting:	
Direct-fired roaster	0.05
Indirect-fired roaster	0.05
Nitrate Fertilizer Manufacture:	
Granulator	0.45
Granulator with dryer and cooler	1.5
Sugar Cane Field Burning	g/m^2 3.4
METALLURGICAL INDUSTRY	
Coke Manufacture:	
Charging	0.015
Coking cycle	0.005
Steel Foundry:	
Electric arc melting	0.1
Open-hearth melting	0.005
MINERAL PRODUCTS INDUSTRY	
Brick Manufacture:	
Gas-fired curing and firing	0.3
Oil-fired curing and firing	0.65
Coal-fired curing and firing	0.75

See footnote at the end of the table.

UNCONTROLLED EMISSION RATES FOR NITROGEN OXIDE SOURCES--Continued

Type of Emission Source		Emission Rate (g/kg)[1]
PETROLEUM INDUSTRY		
Petroleum Refinery:		
Boiler and process heater		
Oil-fired	g/m^3	8274
Gas-fired	g/m^3	3.7
Fluid catalytic cracker (fresh feed)	g/m^3	180
Moving-bed catalytic cracker (fresh feed)	g/m^3	14.3
Compressor internal combustion engine	g/m^3	14.4

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[1] Units other than g/kg are given at the end of the entries immediately preceding numerical values for uncontrolled rates; when controlled rates are known, they are listed by the type of control applied.

REFERENCE

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